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Volume IX

PRODUCTION OF JET FUELS FROM COAL DERIVED LIQUIDS

VOL IX - RESULTS OF BENCH - SCALE AND PILOT PLANT TESTING

MARK FURLONG
JOE FOX
JOE MASIN

AMOCO OIL COMPANY
RESEARCH AND DEVELOPMENT
P.O. BOX 400
NAPERVILLE, IL 60566

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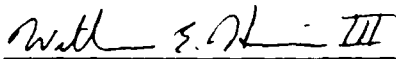
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WILLIAM E. HARRISION III
Project Engineer



CHARLES L. DELANEY, Chief
Fuels Branch
Fuels and Lubrication Division

FOR THE COMMANDER



ROBERT D. SHERRILL, Chief
Fuels and Lubrication Division
Aero Propulsion & Power Laboratory

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SUMMARY

Amoco and Lummus Crest are contracted with the Department of Energy to develop an upgrading scheme for the liquid by-products (tar oil, phenols, and naphtha) produced by the Great Plains Coal Gasification plant in Beulah, North Dakota. These streams are currently burned in the utility boilers and steam superheaters in the Great Plains plant. Tasks 1 through 3 of the contract are complete. Task 1 results were reported previously (AFWAL-TR-87-2042 Volume VI), and the results of Tasks 2 and 3 are reported here.

The objectives of Task 2 are to confirm process simulation results obtained in Task 1, to determine optimum process conditions for operation of the pilot plant in Task 3, and to produce small samples of jet fuels. However, after initial experiments failed to confirm the Task 1 plan, development of a viable process became the primary objective to Task 2. Further bench scale experiments provided a basis for an improved process, established pilot plant conditions for Task 3, and a preliminary design basis for Task 4, and produced small samples of JP-4, JP-8, and JP-8X aviation turbine fuels.

Pilot plant operation in Task 3 confirmed the viability of the Task 2 process by demonstrating extensive recycle of high boiling materials by hydrocracking. Two barrels of JP-8 jet fuel were produced for evaluation by the United States Air Force, and other contractors to the Department of Energy and the Air Force.

Hydrocracking experiments in Task 2 suggested the coal-derived liquids deactivate catalysts more rapidly than petroleum-derived stocks. This should be verified and the cause determined in future studies. The results of Tasks 1 through 3 will be applied to a preliminary process design and to a production run recommendation in Task 4 and 5, respectively.



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FOREWORD

In September 1986, the Fuels Branch of the Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio, commenced an investigation of the potential for production of jet fuel from the liquid by-product streams produced by the gasification of lignite at the Great Plains Gasification Plant located in Beulah, North Dakota. Funding was provided to the department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) to administer the experimental portion of this effort. This report details the effort of Amoco Oil Company, who is a contractor to DOE (DOE Contract Number DE-AC22-87PC90015), conducted a preliminary analysis of upgrading alternatives for the production of turbine fuels from the Great Plains liquid by-product streams. DOE/PETC was funded through Military Interdepartmental Purchase Request (MIPR)-FY1455-86-NO657. Mr. William E. Harrison III was the Air Force Program Manager, Mr. Gary Stiegel was the DOE/PETC Program Manager, and Mark Furlong was the Amoco Program Manager.

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SECTION I

INTRODUCTION

The Great Plains Coal Gasification Plant in Beulah, North Dakota, produces about 145 MM SCF/D of substitute natural gas (SNG) from lignite. The plant also produces three liquid by-products: about 2,900 B/D of tar oil, 830 B/D of crude phenols, and 650 B/D of naphtha. These liquids are all products from the devolatilization of lignite in the Lurgi gasifiers. Currently, the by-products are burned in the plant's boilers and superheaters to produce steam. The economic viability of the plant might be improved by producing marketable products, rather than steam, from these by-product liquids. To this end, Amoco and Lummus Crest, under a contract with the United States Department of Energy, are investigating the technical and economic feasibility of converting the by-product liquids to jet fuels and other saleable products. Jet fuels are of particular interest because of the close proximity of Great Plains to several U.S. Air Force bases, and the obvious strategic interest in maintaining a constant, source of jet fuel for those bases.

SECTION II

PROJECT OVERVIEW

As shown in Figure 1, this project is divided into five major tasks: Process Concept Definition, Bench Scale Testing, Pilot Plant Testing, Preliminary Process Design and Economics, and Production Run Recommendation. The results of Tasks 2 and 3 are reported here.

The first task, Process Concept Definition, includes three subtasks: Liquid By-Product Analysis, Process Modelling and Design, and Economic Modelling. The first of these subtasks (1.1), By-Product Analyses, involves analytical characterizations of samples of each by-product taken at six-week intervals. The results from this program, which provide an indication of the average quality of each stream and the variability of that quality over time, are an important input to the second subtask include limited experimental processing data on the Great Plains by-products by the Western Research Institute (WRI),⁽¹⁾ Amoco's petroleum refining process models and linear programming technology, Lummus' process simulation and design programs and a market analysis of by-products from Great Plains developed by Sinor Consultants.⁽²⁾ In addition, throughout Task 1, ANG Coal Gasification Company provided valuable input and advice on all fronts. The major objective of subtask 1.2 is to produce seven conceptual designs and associated capital and operating costs for facilities to refine the Great Plains by-products. These include designs for maximizing productions of each grade of jet fuel (JP-4, JP-8, JP-8X), designs for profitable schemes which produce the various jet fuel grades, and a scheme for maximizing profits. In subtask 1.3 the results generated by Amoco and Lummus are subjected to economic analysis.

The two products from Tasks 1 were the design and economic results for each of the seven designs and a plan for bench scale testing (Task 2) to confirm any assumptions made in Task 1. The final report for Task 1 was issued by the U.S. Air Force in September 1988.⁽³⁾ Based on the design and economic results from Task 1 and preliminary results from Task 2, the Department of Energy and the Department of Defense decided on a preferred processing scheme for the Great Plains liquids, the "profitable JP-8" case developed in Task 1. Amoco has carried out pilot plant testing (Task 3) of the process design from Tasks 1 and 2 and has provided barrel quantities of product for testing by the United States Air Force and associated contractors. The pilot plant results are being used by Amoco and Lummus to develop a preliminary process design (Task 4) for a plant to upgrade the liquid by-products at Great Plains. Finally, in Task 5, Lummus will suggest existing facilities where the processing scheme might be carried out on a scale sufficient to provide jet fuel for aircraft testing.

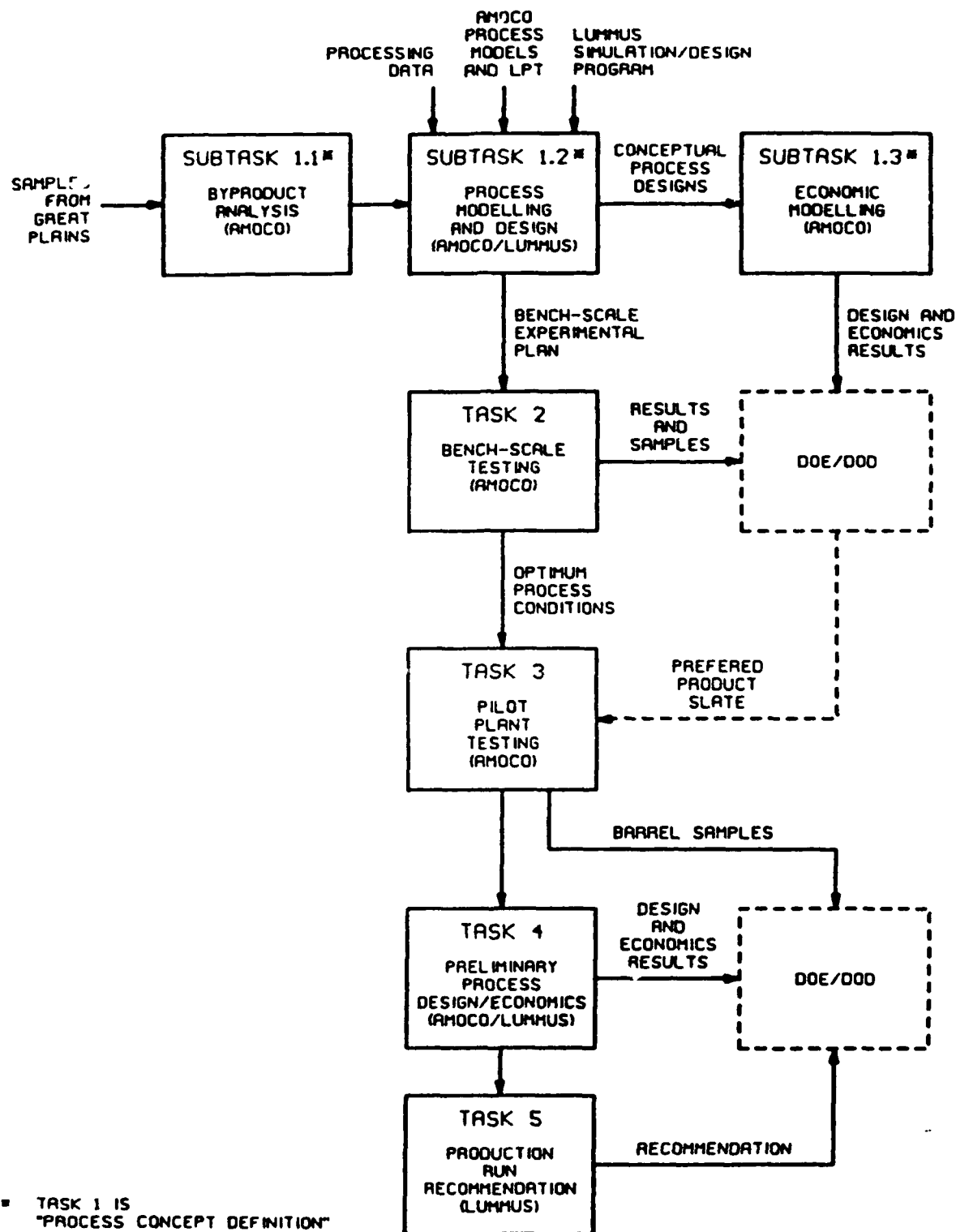


FIGURE 1
PRODUCTION OF JET FUEL
FROM COAL DERIVED LIQUIDS:
AMOCO/LUMMUS ACTIVITIES

SECTION III

SOURCE OF BY-PRODUCT LIQUIDS

Tar oils, crude phenols, and naphtha are produced at the Great Plains Gasification Plant; a schematic of the plant is shown in Figure 2. The plant currently produces about 145 MMSCFD of synthetic natural gas (SNG) from North Dakota lignite. The SNG is composed almost entirely of methane, which is derived mostly from synthesis gas ($H_2 + CO$) produced in the Lurgi Mark IV gasifiers and methanated in downstream reactors. The liquid by-products (tar oil, phenolics, and naphtha) are produced during lignite devolatilization in the gasifiers.

The tar oil and phenolics are condensed from the product gas along with water vapor to form a gas liquor. This condensation takes place in heat exchangers located in the gasifier quench, shift converter, gas cooling, and Rectisol units. The liquor is routed to the gas liquor separation unit, where the tar oil is recovered by gravity separation. The heaviest portion of the tar oil, which contains about 20 percent coal dust, is recycled to the gasifiers. The recycle rate of this "dusty tar" is about 1800 B/D. The remaining tar oil, which contains 2-6 percent dust, is produced at a rate of 2900 B/D. The phenolics are recovered from the gas liquor by extraction with isopropyl ether in the Phenolsolvan unit. The resulting crude phenol stream, which is produced at a rate of about 830 B/D is composed mostly of phenol, cresol, and xlenol, with the remainder being water and neutral oils. The naphtha is condensed from the gasifier raw gas by contacting the stream with cold methanol in the Rectisol unit. The naphtha is produced at a rate of 650 B/D.

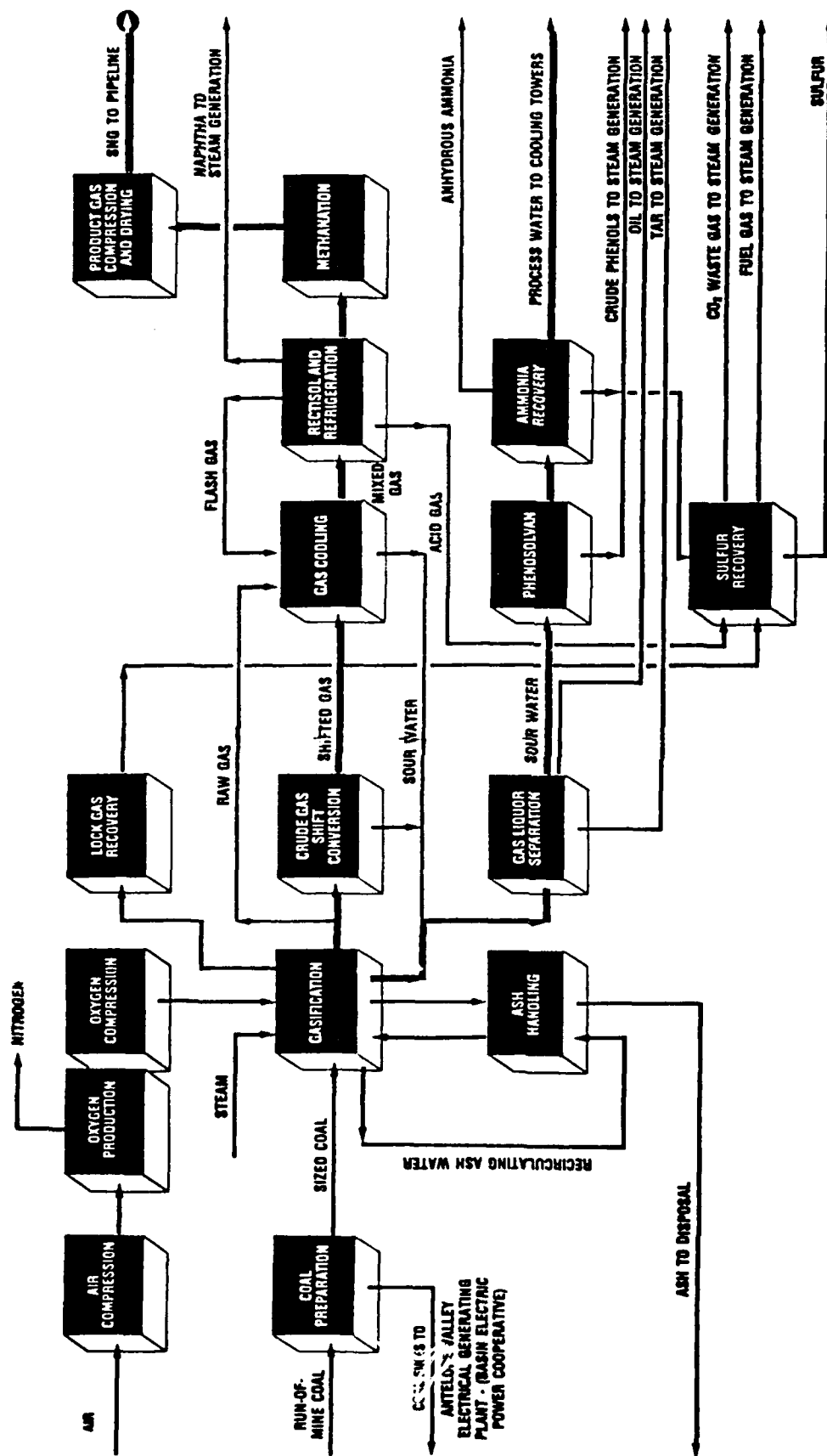


FIGURE 2. GREAT PLAINS GASIFICATION PROCESS BLOCK FLOW DIAGRAM

SECTION IV

TASK 2 RESULTS

As outlined in the Task 1 recommendations (3) and the project contract (4), the objectives of Task 2 are to confirm process simulation model results obtained in Task 1, to determine optimum process conditions for operation of the pilot plant in Task 3, and to produce small samples of jet fuels.

Experiments to confirm the Task 1 plan showed that the recommended process could not produce specification jet fuels. Accordingly, bench-scale experiments to develop a viable process became the primary objective of Task 2. Optimization, particularly data analysis confirming the reaction kinetics used in the Task 1 models, was not completed. However, raw data necessary for this analysis are presented here, and were used to specify process design conditions.

An overview of this process development work is presented below, followed by more detailed discussions of the experimental procedures and results which defined conditions for a working tar-oil conversion process. Analyses of the small samples of JP-4, JP-8, and JP-8X jet fuels produced during these runs are also discussed.

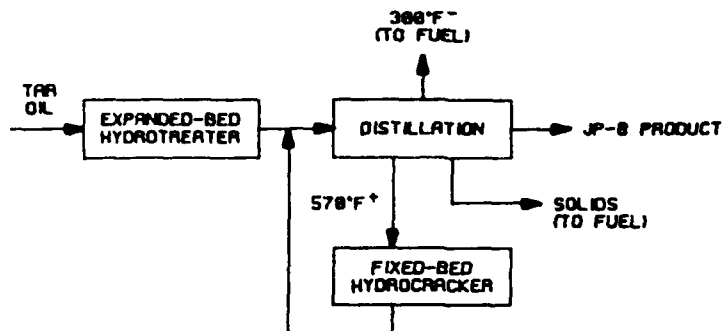
A. Overview of Process Development Work

As a part of Task 1, a process for the production of jet fuel from tar oil was developed in the "Profitable JP-8 Case". The Task 1 recommendation was to process the tar oil in an expanded-bed hydrotreater to lower aromatics content and nitrogen levels in the feed and then to hydrocrack the material boiling over 570°F to extinction in a fixed-bed hydrocracker (Figure 3). The expanded-bed hydrotreater was recommended to handle the high solids content in the tar oil and high releases expected during hydrotreating.

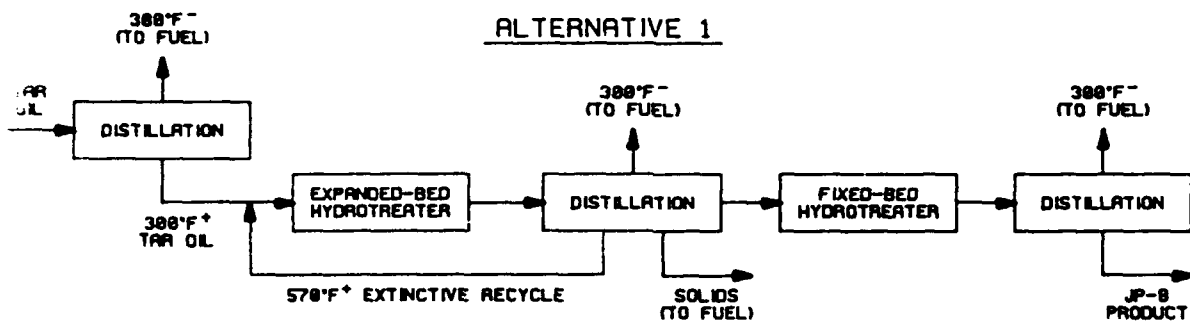
The initial goal of Task 2 was to verify this scheme recommended in Task 1 and to provide data on appropriate operating conditions and product yields and qualities. Selection of the expanded-bed hydrotreater for the first stage was verified when attempts to remove the solids by distillation resulted in losses of 25 percent of the tar oil to decomposition in the still pot. Since the solids could not be removed by distillation without significant losses and since fixed-bed reactors cannot handle solids without plugging, an expanded-bed reactor is required for the first stage of hydrotreating. However, the process is not feasible as recommended. The expanded-bed hydrotreater, although fine for handling solids and high heat releases, has significant backmixing and cannot lower the aromatics content of the feed sufficiently to meet jet fuel specifications. Consequently, alternative processes were developed.

Alternatives 1 through 3, shown in Figure 3, represent progressively more severe and more capital intensive approaches for the conversion of the tar oil to JP-8. All three cases contain a distillation pretreatment step to remove water and materials boiling below 300°F from the tar oil before

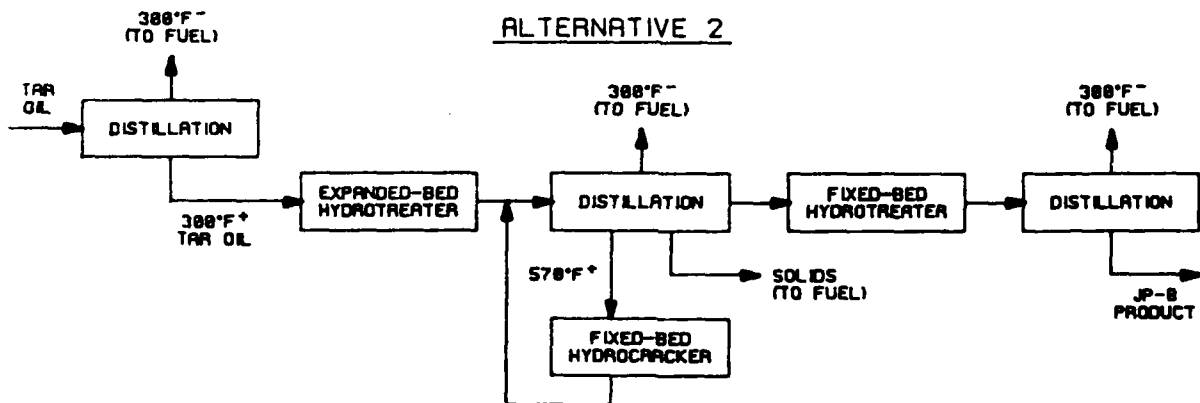
TASK 1 RECOMMENDATION



ALTERNATIVE 1



ALTERNATIVE 2



ALTERNATIVE 3

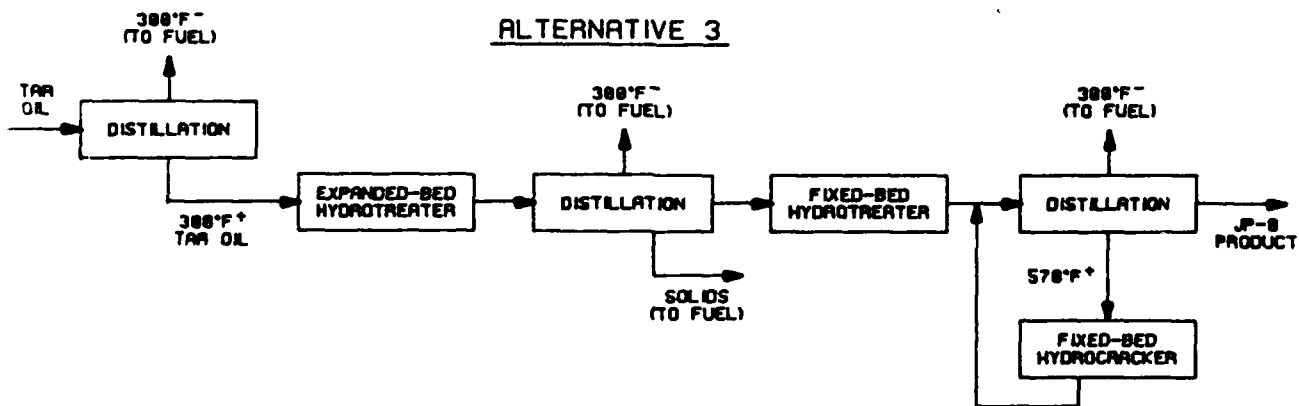


FIGURE 3. TAR OIL PROCESSING ALTERNATIVES

hydroprocessing. This reduces first-stage hydrotreater capacity. Removal of the lighter materials lowers the total hydrogen consumptions much as 4 percent. Furthermore, the light products from the 300°F minus feed would be unsuitable for jet fuel. Process optimization may recommend taking a heavier cut which could improve the economics.

Of the three alternatives, Alternative 1 is the simplest, requiring only two stages of hydrotreating and no hydrocracker. In Alternative 1, the first stage hydrotreater operates in a recycle mode. The material boiling over 570°F is recycled back to the expanded bed hydrotreater to lower its boiling range. After distillation to remove the light ends and solids, neither of which are suitable as jet fuel substituents, the remaining liquids are treated over a fixed-bed hydrotreater to further lower the aromatics and nitrogen contents to meet jet fuel specifications. Alternative 2 is similar to the Task 1 recommendation with the addition of a second hydrotreater after the hydrocracking stage. The second hydrotreater will lower the nitrogen and aromatics contents of the product to jet fuel specifications. Finally, Alternative 3 requires two stages of hydrotreating, followed by a hydrocracker. The first, expanded-bed hydrotreater lowers the nitrogen and aromatics contents and saturates olefins in the tar oil which permits solids removal by distillation without significant losses to retrograde reactions, which the raw tar oil demonstrated. After the first stage of hydrotreating, the solids and light ends are stripped from the hydrotreated product and sent to a second-stage, fixed-bed hydrotreater to further reduce the nitrogen level and aromatics content. Finally, the 570°F+ fraction is hydrocracked to extinction in a final, hydrocracker stage.

Alternative 1 was tested first, since it has the lowest capital cost and a hydrocracker is not required. Instead of lowering the boiling point to jet fuel range by hydrocracking, the 550°F+ material is recycled to extinction in the first-stage hydrotreater. Bench scale testing showed that there was virtually no conversion of the 550°F recycle material in the recycle mode. Although 35 percent of the fresh feed was converted in one pass at 0.6 weight-hourly space velocity (WHSV), the recycle material was not converted in the hydrotreater. Even at space velocities as low as 0.2 and 0.1 conversion of the recycle stream was undetectable. Alternative 1, then, was not effective.

Alternative 2 was tested next as it is the next most cost effective design. Alternative 2 requires a fixed-bed hydrocracker between the two hydrotreater stages used in Alternative 1. Because the heavy materials are hydrocracked first the fixed-bed hydrotreater can operate at relatively mild conditions and will be less expensive than a second hydrotreater installed in front of the hydrocracker (as in Alternative 3).

Alternative 2 failed because rapid catalyst deactivation occurred in the hydrocracker with hydrotreated 550°F+ tar oil containing as little as 200 ppm nitrogen. Some petroleum hydrocrackers are routinely operated at these nitrogen levels. This deactivation may be caused by nitrogen-containing materials peculiar to coal-derived liquids which poison the active sites on the catalyst. The nitrogen compounds in the coal-derived material are different when compared to petroleum-derived stocks of similar boiling range. A comparative examination of nitrogen compound types in the tar oil and petroleum feedstocks might explain deactivation and differences in

hydrocracking of the two feedstock types. For example, the addition of denitrogenation catalyst above the hydrocracking catalyst beds may make Alternative 2 viable.

Alternative 3 is the most severe of the alternatives and was successful at converting the tar oil to jet fuel. Since the fixed-bed hydrotreater processes the entire expanded-bed effluent stream the size of the fixed-bed hydrotreater is nearly doubled relative to Alternative 2. The second stage hydrotreater lowers the nitrogen level to 10 ppm before the hydrocracker, which gives stable hydrocracker operation and reasonable hydrocracker catalyst life. It may be possible to install hydrotreater beds above the hydrocracker beds in a single vessel, eliminating the separate fixed-bed hydrotreater. The advantage of Alternative 3 is that less hydrogen is consumed and better reactor control is possible with this design, than a system with denitrogenation beds added to the hydrocracker (modification to Alternative 2).

Compared with the scheme described in Task 1, Alternatives 2 and 3 would be considerably more expensive, as there are two more distillation and one more hydrotreater involved. However, the bench-scale and pilot-plant work verified the need for the more severe design of Alternative 3. Although it is more capital intensive, Alternative 3 has better operability, more flexibility, and the capability to process the tar oil to meet JP-8 specifications.

The experimentally-verified version of Alternative 3 uses nickel-molybdenum-phosphorous on alumina catalyst operating at 760°F and 2,000 psig for denitrogenation in the first-stage hydrotreater. The second-stage operates at the same conditions with nickel-tungsten-phosphorous on alumina catalyst to promote aromatics saturation while removing most of the remaining nitrogen. The hydrocracker uses a commercial nickel-tungsten catalyst on "y" sieve. More detailed catalyst compositions are given below.

Figure 4 and Table I show the experimentally-verified process based on Alternative 3. This is the recommended basis for the preliminary process design to be developed in Task 4 of this project and the basis for production of the larger samples of JP-8 for Task 3.

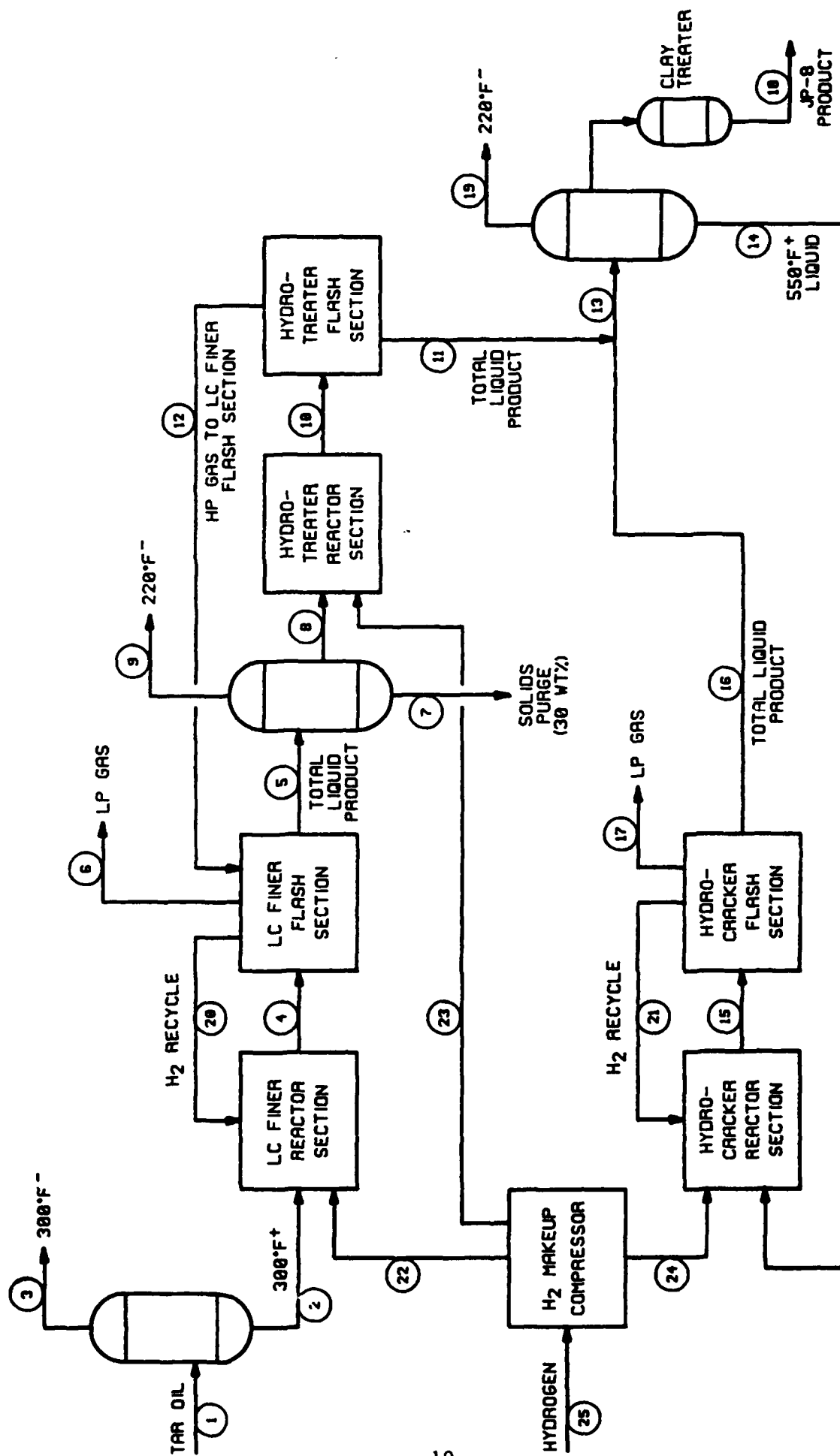


FIGURE 4
RECOMMENDED PROCESS DESIGN BASIS

TABLE I

MATERIAL BALANCE FOR RECOMMENDED PROCESS

| Stream No. | <u>1</u> | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> | <u>6</u> | <u>7</u> | <u>8</u> | <u>9</u> |
|---------------------------------|----------|-------------------|-------------------|----------------------|-----------------------|----------------|-----------------|---------------------------|------------------------|
| Stream Description | Tar Oil | 300°F+ Tar Oil | 300°F- Tar Oil | LC Finer Effluent | LC Finer Tot. Liq. | LP Gas Vent | Solids Purge | Hydro- Treater Feed | Light Ends Purge |
| Components, lbs/hr | | | | | | | | | |
| Carbon | 40,077 | 38,763 | 1,314 | | 37,508 | 1,751 | 1,094 | 35,339 | 1,075 |
| Hydrogen | 4,090 | 3,936 | 154 | | 5,333 | 1,051 | 122 | 5,000 | 211 |
| Nitrogen | 385 | 333 | 52 | | 8 | 333 | | 8 | |
| Sulfur | 257 | 226 | 31 | | 4 | 226 | | 4 | |
| Oxygen | 2,861 | 2,505 | 356 | | 18 | 2,505 | | 18 | |
| Solids | Incl. | Incl. | | | 521 | | 521 | | |
| Total | 47,670 | 45,763 | 1,907 | | 43,392 | 5,866 | 1,737 | 40,369 | 1,286 |
| Flow Rate, gpm | | | | | | | | | |
| Temperature, °F | | | | | | | | | |
| Pressure, psia | | | | | | | | | |
| Viscosity Liq., cs | | | | | | | | | |
| Sp. Gr. Liquid | 1.015 | 1.028 | | | 0.881 | | | 0.879 | |
| Gas Density, lb/ft ³ | | | | | | | | | |
| Vapor Pressure, psia | | | | | | | | | |

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TABLE I (Cont.)

MATERIAL BALANCE FOR RECOMMENDED PROCESS

| Stream No. | <u>10</u> | <u>11</u> | <u>12</u> | <u>13</u> | <u>14</u> | <u>15</u> | <u>16</u> | <u>17</u> | <u>18</u> |
|---------------------------------|-------------------------------|--|-------------------------------|------------------------|---------------------------|-------------------------------|--|----------------|-----------------|
| Stream Description | Hydro- treater Effluent | Hydro- treater Tot.Liq. Product | Hydro- treater Vent Gas | Fraction- ator Feed | Hydro- Cracker Feed | Hydro- Cracker Effluent | Hydro- Cracker Tot.Liq. Product | LP Gas Vent | JP-8 Product |
| Components, lbs/hr | | | | | | | | | |
| Carbon | | 34,843 | 496 | 51,140 | 17,397 | | 16,297 | 1,100 | 31,976 |
| Hydrogen | | 5,207 | 839 | 7,645 | 2,241 | | 2,438 | 339 | 5,033 |
| Nitrogen | | | 8 | | | | | | |
| Sulfur | | | 4 | | | | | | |
| Oxygen | | | 18 | | | | | | |
| Solids | | | | | | | | | |
| Total | | 40,050 | 1,365 | 58,785 | 19,638 | | 18,735 | 1,439 | 37,009 |
| Flow Rate, gpm | | | | | | | | | |
| Temperature, °F | | | | | | | | | |
| Pressure, psig | | | | | | | | | |
| Viscosity Liq., cs | | | | | | | | | |
| Sp. Gr. Liquid | | | | | | | | | |
| Gas Density, lb/ft ³ | | | | | | | | | |
| Vapor Pressure, psia | | | | | | | | | |

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TABLE I (Cont.)

MATERIAL BALANCE FOR RECOMMENDED PROCESS

| Stream No. | 19 | 20 | 21 | 22 | 23 | 24 | 25 |
|---------------------------------|------------------------|------------------------------------|---|-------------------------------|--|--|--------------------------------|
| Stream Description | Light Ends Purge | LC Finer H ₂ Recycle | Hydro- cracker H ₂ Recycle | H ₂ To LC Finer | H ₂ To Hydro- treater | H ₂ To Hydro- cracker | Total H ₂ Makeup |
| Components, lbs/hr | | | | | | | |
| Carbon | 1,767 | | | | | | |
| Hydrogen | 371 | | | 1,609 | 1,046 | 536 | 3,191 |
| Nitrogen | | | | | | | |
| Sulfur | | | | | | | |
| Oxygen | | | | | | | |
| Solids | | | | | | | |
| Total | 2,138 | | | 1,609 | 1,046 | 536 | 3,191 |
| Flow Rate, gpm | | | | | | | |
| Temperature, °F | | | | | | | |
| Pressure, psig | | | | | | | |
| Viscosity, Liq., cs | | | | | | | |
| Sp. Gr. Liquid | | | | | | | |
| Gas Density, lb/ft ³ | | | | | | | |
| Vapor Pressure, psia | | | | | | | |

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B. Distillation Pretreatment of Tar Oil Feed

Table 2 shows analyses of tar oil before and after distillation to remove water and low-boiling (<300°F) hydrocarbons. The 300°F cut point represented less than 5 percent of the as-received tar oil, but removed about two-thirds of the water and most of the low-boiling hydrocarbons. These low-boiling hydrocarbons included about 10 percent of the nitrogen and oxygen, 8 percent of the sulfur, and 3 percent of the "aromatics" (presumably volatile pyridinics, oxygenates, and mercaptans).

Distillation pretreatment decreases consumption of hydrogen that would otherwise be required to convert these low-boiling heteroatomic compounds to NH₃, H₂S, and light hydrocarbons. All of these consume more hydrogen than do aromatics saturation reactions. Pretreatment decreases overall hydrogen consumption by about 4 percent, reducing the cost of JP-8 product by about 2 percent.

C. Hydrotreating Scoping Runs

As-received tar oil from the Great Plains plant was hydrotreated in a bench-scale autoclave reactor to determine heat release and to provide denitrogenation kinetic data. Table 3 shows selected properties of tar oil and petroleum heavy virgin gas oil feeds used in these experiments. Whole tar oil taken from Great Plains on November 16, 1987, was the feed for these experiments. Later runs on other units used tar oil taken on January 18, 1988, distilled to remove materials boiling below 300°F.

Whole tar oil was hydrotreated in an automated, high pressure isothermal basket autoclave reactor system, shown schematically in Figure 5. The reactor, Figure 6, is a nominal one-liter heavy wall vessel with a center-positioned magnetically-driven mixer designed to minimize solids accumulation on the catalyst. A cylindrical basket suspended between the vessel wall and mixer holds up to 150 cc of catalyst.

126 grams of Shell 424 catalyst, 1/16 inch extrudate with an average length of about 1/4 inch, was sulfided then conditioned for about 120 hours with a standard petroleum heavy vacuum gas oil (HVGO) before a base-case run to monitor catalyst activity. Table 4 shows the catalyst composition for all three of the reactor systems.

Table 5 shows the run conditions and corresponding product analyses, and Table 6 summarizes material balances for the runs, closed by mathematically adjusting feed input to provide carbon balance. For all runs, temperature and system pressure were held constant at 720°F and 1,800 psig while varying the apparent weight-hourly space velocity (WHSV) between 0.5 and 4. Baseline runs with HVGO feed before and after the tar oil runs showed that catalyst remained suitably active for these experiments so that no adjustments for catalyst activity decline were necessary.

The material balance results show that hydrogen uptake, C₁-C₄ gas production, heteroatom gas make, denitrogenation, and desulfurization all increased as expected with decreased space velocity. However, the desulfurization results are somewhat erratic, suggesting that hydrogen sulfide may have recombined

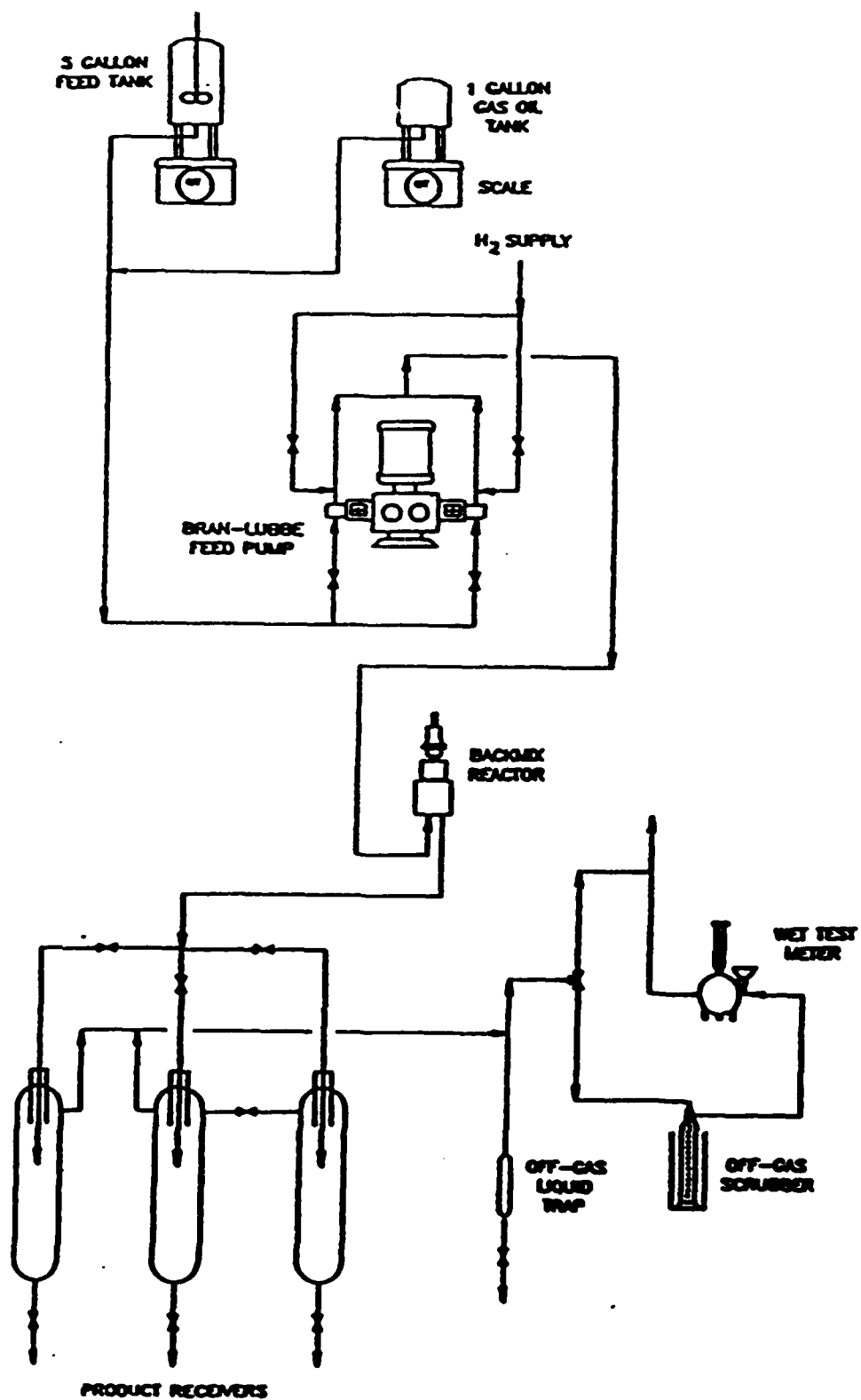


FIGURE 5
HYDROTREATING PILOT PLANT--BASKET AUTOCLAVE

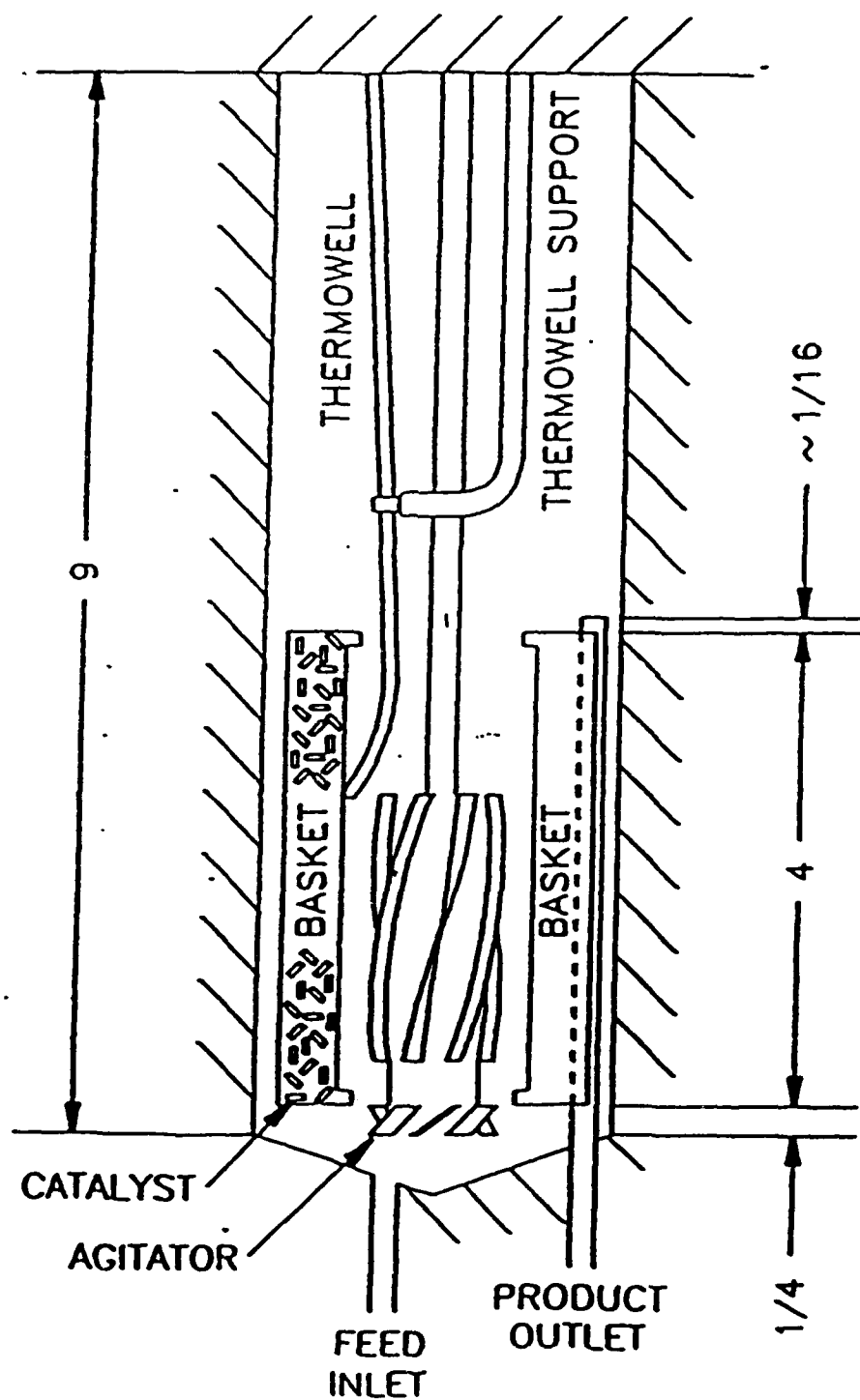


FIGURE 6

BASKET AUTOCLAVE REACTOR INTERNALS

TABLE 2
SELECTED PROPERTIES OF TAR OIL FEED
BEFORE AND AFTER DISTILLATION PRETREATMENT

| Sample Description: | 1/18/88 Whole Tar Oil | 1/18/88 300F+ Tar Oil |
|----------------------------------|--------------------------|--------------------------|
| Elemental Analysis, As Received: | | |
| Water, wt.% | 1.55 | 0.59 |
| Elemental Analysis, Dry Basis: | | |
| Carbon, wt.% | 84.07 | 84.71 |
| Hydrogen, wt.% | 8.58 | 8.60 |
| Nitrogen, ppm | 8,065 | 7,283 |
| Sulfur, ppm | 5,383 | 4,929 |
| Oxygen, ppm (diff.) | 60,012 | 54,739 |
| Atomic H/C Ratio | 1.22 | 1.21 |
| API Gravity | 7.9 | 6.2 |
| Specific Gravity | 1.015 | 1.028 |
| Mass Spectral Results, wt.% | | |
| Saturates | 36.3 | 37.9 |
| Paraffins | 8.3 | 10.3 |
| NCond. Cycp'fins | 6.5 | 7.6 |
| Cond. 2-Ring " | 0.0 | 0.0 |
| Cond. 3-Ring " | 21.6 | 20.0 |
| Isoparaffins | 0.0 | 0.0 |
| Naphthenes | 0.0 | 0.0 |
| Aromatics | 63.7 | 62.1 |
| Mono Species | 35.9 | 34.3 |
| Di " | 19.1 | 19.5 |
| Tri " | 3.1 | 2.5 |
| Tetra " | 1.0 | 0.8 |
| Penta " | 0.5 | 0.4 |
| Thiopheno " | 3.9 | 4.3 |
| unidentified | 0.3 | 0.3 |
| Total CA, wt. % | 27.1 | 27.4 |

G. C. Simulated Distillation, ASTM Method D-2887

| Weight % Distilled | Temperature, F | |
|--------------------|----------------|-------|
| IBP | 167 | 279 |
| 5 | 281 | 336 |
| 10 | 338 | 371 |
| 20 | 390 | 414 |
| 30 | 440 | 468 |
| 40 | 486 | 498 |
| 50 | 544 | 556 |
| 60 | 586 | 603 |
| 70 | 674 | 683 |
| 80 | 760 | 765 |
| 90 | 881 | 877 |
| 95 | 961 | 948 |
| FBP | 1,018 | 1,018 |

TABLE 3
SELECTED PROPERTIES OF TAR OIL AND
AMOCO HEAVY VACUUM GAS OIL

| Sample Description: | Tar Oil 11/16/87 | HVGO |
|--------------------------------|---------------------|--------|
| Water, wt.% | 1.41 | 0.00 |
| Elemental Analysis, Dry Basis: | | |
| Carbon, wt.% | 84.19 | 85.28 |
| Hydrogen, wt.% | 8.56 | 11.79 |
| Nitrogen, ppm | 8,297 | 1,338 |
| Sulfur, ppm | 4,730 | 28,200 |
| Oxygen, ppm (diff.) | 59,462 | -238 |
| Atomic H/C Ratio | 1.21 | 1.65 |
| API Gravity | 7.8 | 19.8 |
| Specific Gravity | 1.016 | 0.935 |
| Chlorides, ppm | 1.0 | -- |
| Ash Oxide, wt. % | 0.03 | -- |
| Filtered Solids, wt.% | 0.16 | -- |
| PSD (Microtrac), % | | |
| <4 microns | 7.4 | -- |
| 4.4-6.6 | 6.8 | -- |
| 6.6-9.4 | 9.0 | -- |
| 9.4-13 | 10.4 | -- |
| 13-19 | 13.4 | -- |
| 19-27 | 11.0 | -- |
| >27 microns | 41.5 | -- |

TABLE 4
TYPICAL CATALYST PROPERTIES

| | <u>First Hydrotreater</u> | <u>Second Hydrotreater</u> | <u>Hydrocracker</u> |
|----------------------------------|-------------------------------|--------------------------------|-----------------------|
| Supplier No. | Shell 424 | Shell 354 | Davison SMR 6-1881 |
| Shape | Tri-lobed | Tri-lobed | Cylindrical |
| Nominal Size, in. | 1/16 | 1/8 | 1/8 |
| Composition, wt.% | | | |
| Nickel | 3.0 | 3.0 | 1.6 |
| Tungsten | 0.0 | 25.0 | 14.2 |
| Molybdenum | 13.0 | 0.0 | 0.0 |
| Phosphorus | -- | 2.5 | 0.0 |
| Physical Properties | | | |
| Surface Area, m ² /gm | 162 | 135 | 325 |
| Pore Volume, ml/gm | 0.47 | 0.39 | 0.42 |
| Support | Alumina | Alumina | "γ" Sieve |

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TABLE 5
HYDROTREATING SCOPING EXPERIMENTS--
RUN CONDITIONS AND PRODUCT ANALYSES

| Run No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--------------------------------|--------|---------|---------|---------|---------|---------|--------|
| Feed | HVGO | Tar Oil | Tar Oil | Tar Oil | Tar Oil | Tar Oil | HVGO |
| Nominal WHSV | 2.2 | 4.6 | 1.9 | 2.3 | 1.0 | 0.5 | 2.2 |
| Temperature, F | 720 | 720 | 720 | 720 | 720 | 720 | 720 |
| Pressure, psig | 1,800 | 1,800 | 1,800 | 1,800 | 1,800 | 1,800 | 1,800 |
| Water, wt. % | 0.01 | 0.41 | 0.11 | 0.15 | 0.04 | 0.00 | 0.07 |
| Elemental Analysis, Dry Basis: | | | | | | | |
| Carbon, wt. % | 86.84 | 86.95 | 87.23 | 87.15 | 87.55 | 87.76 | 86.80 |
| Hydrogen, wt. % | 12.73 | 10.67 | 11.23 | 11.15 | 11.62 | 11.81 | 12.63 |
| Nitrogen, ppm | 300 | 4,749 | 3,254 | 3,205 | 1,721 | 980 | 550 |
| Sulfur, ppm | 3,839 | 889 | 2,359 | 800 | 958 | 665 | 6,364 |
| Oxygen, ppm (diff) | 153 | 18,215 | 9,827 | 12,987 | 5,660 | 2,655 | -- |
| Atomic H/C Ratio | 1.75 | 1.46 | 1.53 | 1.52 | 1.58 | 1.60 | 1.73 |
| API Gravity | 25.9 | 23.0 | 26.2 | 25.4 | 28.8 | 29.8 | 25.3 |
| Specific Gravity | 0.8990 | 0.9190 | 0.8974 | 0.9016 | 0.8827 | 0.8775 | 0.9024 |
| Mass Spectral Results, wt. % | | | | | | | |
| Saturates | 32.8 | 44.9 | 49.7 | 48.4 | 52.6 | 54.9 | -- |
| Paraffins | 32.8 | 12.8 | 12.7 | 12.2 | 13.0 | 12.9 | -- |
| NCond. Cycp'fins | -- | 20.5 | 25.3 | 24.4 | 26.8 | 28.3 | -- |
| Cond. 2-Ring " | -- | 3.6 | 5.4 | 5.5 | 7.5 | 8.7 | -- |
| Cond. 3-Ring " | -- | 8.0 | 6.2 | 6.3 | 5.3 | 5.0 | -- |
| Isoparaffins | -- | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | -- |
| Naphthenes | -- | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | -- |
| Aromatics | 7.0 | 55.1 | 50.3 | 51.6 | 47.4 | 45.1 | -- |
| Mono Species | -- | 38.9 | 38.6 | 38.9 | 37.3 | 36.2 | -- |
| Di " | -- | 12.5 | 9.4 | 10.0 | 7.3 | 6.7 | -- |
| Tri " | -- | 2.2 | 1.9 | 1.8 | 1.5 | 1.5 | -- |
| Tetra " | -- | 0.4 | 0.2 | 0.2 | 0.5 | 0.2 | -- |
| Penta " | -- | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | -- |
| Thiopheno " | -- | 0.6 | 0.1 | 0.4 | 0.5 | 0.2 | -- |
| Unidentified | -- | 0.3 | 0.0 | 0.2 | 0.1 | 0.1 | -- |
| Total CA, wt. % | -- | 21.5 | 18.8 | 19.9 | 20.7 | 19.7 | -- |

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TABLE 6

HYDROTREATING SCOPING EXPERIMENTS--
MATERIAL BALANCE SUMMARIES AND HEAT RELEASE

| Run No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--------------------------------|------------|------------|------------|------------|------------|------------|------------|
| Feed | HVGO | Tar Oil | Tar Oil | Tar Oil | Tar Oil | Tar Oil | HVGO |
| Nominal WHSV Temperature, F | 2.2 720 | 4.6 720 | 1.9 720 | 2.3 720 | 1.0 720 | 0.5 720 | 2.2 720 |
| Yield Summary, wt. % | | | | | | | |
| Hydrogen | -0.91 | -2.40 | -3.05 | -2.87 | -3.48 | -3.69 | -0.80 |
| Heteroatom Gas | 2.72 | 5.41 | 6.40 | 5.64 | 7.28 | 7.70 | 2.43 |
| C1 - C4 Gas | 0.29 | 0.16 | 0.18 | 0.16 | 0.22 | 0.23 | 0.28 |
| C5+ Liquid | 97.94 | 102.97 | 103.37 | 132.53 | 97.73 | 103.59 | 98.15 |
| Total | 100.04 | 106.14 | 106.89 | 135.46 | 101.75 | 107.83 | 100.06 |
| Hydrogen, SCFB | 562 | 1,608 | 2,044 | 1,925 | 2,334 | 2,472 | 493 |
| H atom gas, SCFB | 104 | 393 | 474 | 412 | 536 | 566 | 92 |
| C1-C4 Gas, SCFB | 9 | 6 | 6 | 6 | 8 | 9 | 9 |
| Conversion, wt. % | | | | | | | |
| Denitrogenation | 78.0 | 41.1 | 59.6 | 48.9 | 79.8 | 87.8 | 59.7 |
| Desulfurization | 86.7 | 80.7 | 48.6 | 77.6 | 80.2 | 85.4 | 77.9 |
| Heat of Reaction, BTU/Bbl* | | | | | | | |
| Denitrogenation | 2,915 | 10,338 | 14,978 | 12,286 | 20,057 | 22,075 | 2,228 |
| Desulfurization | 19,870 | 3,368 | 2,028 | 3,240 | 3,349 | 3,568 | 17,851 |
| Deoxygenation | 0 | 48,037 | 58,188 | 49,857 | 63,624 | 66,902 | 0 |
| Saturation | 20,066 | 61,685 | 82,454 | 84,272 | 92,721 | 97,757 | 17,515 |
| Total | 42,851 | 123,429 | 157,648 | 149,655 | 179,752 | 190,302 | 37,594 |

* 85 BTU/SCF of H2 consumed for saturation, 70 for other reactions.

with product in the receivers. (All samples were washed with zinc chloride solution before analysis to remove dissolved H_2S and NH_3 .)

Heat release was calculated for each run based on hydrogen consumption using 70 BTU/SCF for removal of nitrogen, oxygen, and sulfur, and 85 BTU/SCF for aromatics saturation reactions. For tar oil, the latter value is probably low because it accounts only for aromatics saturation; heats of reaction for saturation of olefins, about 140 BTU/SCF, were not included. Table 5 shows that substantially more heat is released for tar oil hydrogenation than for Amoco's standard HVGO feed.

Hydrogen consumption ranged from 1,600 to 2,500 SCFB, substantially more than 1,400 SCFB for petroleum resid hydroprocessing where expanded-bed reactors facilitate temperature control. Expanded-bed reactors will be necessary for temperature control in commercial tar oil hydrotreating. Because this reactor type can tolerate solids, pretreatment of feed for solids removal is avoided. However, removal of water and light ends upstream of the hydrotreater is recommended, as discussed in Section IV-B.

D. Hydrotreating Experiments

Figure 7 shows the automated, high pressure, isothermal bench-scale unit used to study conditions for first-stage hydrotreating. The reactor, a heavy-wall tube of type 304 stainless steel, 0.625 inch I.D. by 30.5 inches long, fitted with a center-mounted 1/8-inch thermowell, is enclosed by a 1-inch pipe wrapped with electrical heaters which serves as a four-zone furnace. A Ruska pump controls the oil rate and a Brooks mass flow meter the hydrogen rate. Piping was arranged for upflow of oil and hydrogen providing rough simulation of an expanded-bed reactor. Two high-pressure receivers collect product at reactor pressure. Reactor off gas exits the receivers via a pressure control valve, scrubber, and wet test meter.

102 grams of Shell 424 catalyst, 1/16 inch extrudate with an average length of about 1/4 inch, was sulfided then conditioned for about 735 hours with tar oil before a base-case run (Run 3) to monitor catalyst activity decline. Table 4 shows the catalyst composition.

Figure 8 shows the partial factorial experimental design used to study removal of aromatics, nitrogen, and the other heteroatoms from 300°F+ tar oil. Reaction temperatures ranged from 670 to 760°F, pressure from 1,800 to 2,000 psig, and weight-hourly space velocities from 0.6 to 1.2. Table 7 lists conditions and product analyses for each run, and Table 8 summarizes the material balances, closed by adjusting feed input to provide carbon balance.

In the process recommended in Task 1, the high boiling fraction of hydrotreated product is hydrocracked and blended with the lighter hydrotreater fraction to yield specification jet fuel product (containing less than 25 percent aromatics). Table 7 shows that about 65 percent of the lowest aromatics content hydrotreater product (Run 8) boils below 550°F, in the JP-8 fuel range. However, Table 9 shows that this fraction contains about 39 percent aromatics. Even if the higher boiling fraction were hydrocracked to aromatics-free material, the final JP-8 product would still contain over 25 percent aromatics after blending. Light ends removal, necessary to meet

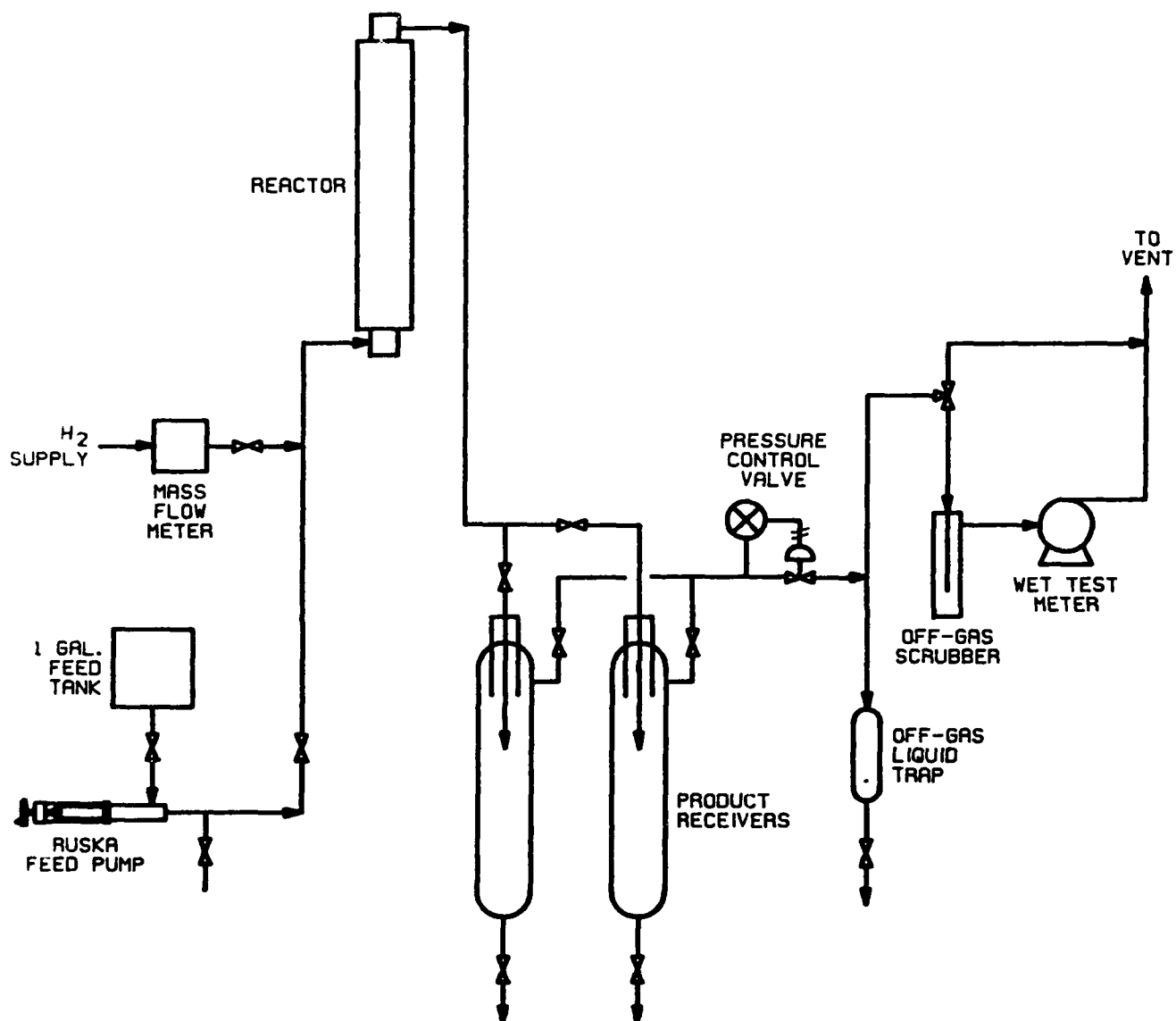
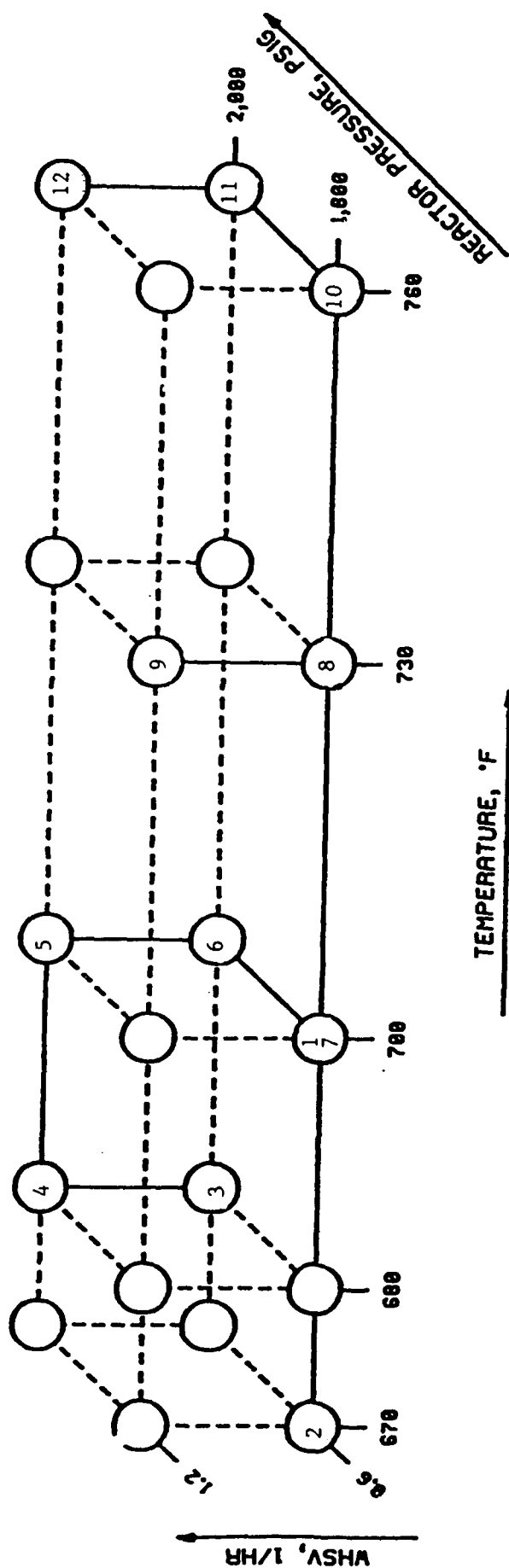


FIGURE 7

HYDROTREATING PILOT PLANT--FIRST HYDROTREATER

④ RUN NUMBER



TEMPERATURE, °F

FIGURE 8
EXPERIMENTAL PROGRAM FOR FIRST HYDROTREATER

TABLE 7

FIRST HYDROTREAT--RUN CONDITIONS AND PRODUCT ANALYSES

| Run No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|--------|--------|--------|--------|--------|--------|--------|-----------------|--------|--------|--------|--------|
| Nominal WHSV | 0.6 | 0.6 | 0.6 | 1.2 | 1.2 | 0.6 | 0.6 | 0.6 | 1.2 | 2.6 | 0.6 | 1.2 |
| Temperature, °F | 700 | 646 | 680 | 680 | 700 | 700 | 700 | 730 | 730 | 760 | 2,000 | 2,000 |
| Pressure, psig | 1,800 | 1,800 | 2,000 | 2,000 | 2,000 | 2,000 | 1,800 | 1,800 | 1,800 | 1,800 | 2,000 | 2,000 |
| Water, wt. % | 0.06 | 0.13 | 0.07 | 0.18 | 0.09 | 0.03 | 0.05 | 0.02 | 0.06 | 0.05 | 0.05 | 0.04 |
| Elemental Analysis, Dry Basis: | | | | | | | | | | | | |
| Carbon, wt. % | 88.07 | 87.11 | 87.34 | 87.26 | 86.93 | 88.18 | 87.88 | 87.64 | 87.96 | 88.13 | 88.06 | 88.06 |
| Hydrogen, wt. % | 11.66 | 11.27 | 11.46 | 11.10 | 11.28 | 12.06 | 11.94 | 12.16 | 11.50 | 11.92 | 12.13 | 11.92 |
| Nitrogen, ppm | 1,901 | 2,653 | 1,951 | 3,166 | 2,382 | 542 | 2,211 | 210 | 1,161 | 180 | 180 | 480 |
| Sulfur, ppm | 693 | 219 | 61 | 132 | 100 | 39 | 192 | 53 | 148 | 102 | 25 | 85 |
| Oxygen, ppm | 2,367 | 5,844 | 4,078 | 7,100 | 6,500 | 1,833 | 4,456 | 1,122 | 3,567 | -364 | -364 | 1,544 |
| Atomic H/C Ratio | 1.58 | 1.54 | 1.59 | 1.52 | 1.55 | 1.63 | 1.56 | 1.65 | 1.56 | 1.61 | 1.64 | 1.61 |
| API Gravity | 26.1 | 24.1 | 26.0 | 22.3 | 24.3 | 28.5 | 25.9 | 30.0 | 25.1 | 30.0 | 30.7 | 28.7 |
| Specific Gravity | 0.8978 | 0.9092 | 0.8986 | 0.9200 | 0.9081 | 0.8845 | 0.8987 | 0.8760 | 0.9033 | 0.8762 | 0.8726 | 0.8834 |
| Mass Spectral Results, wt. % | | | | | | | | | | | | |
| Saturates | 53.4 | 50.9 | 54.2 | 49.5 | 51.1 | 56.8 | 51.7 | 58.2 | 48.9 | 55.4 | 56.7 | 53.0 |
| Paraffins | 9.2 | 12.7 | 8.2 | 12.5 | 11.4 | 9.5 | 9.7 | 11.1 | 11.2 | 12.3 | 12.3 | 10.7 |
| NCond. Cyc'ring | 30.6 | 23.9 | 31.9 | 22.5 | 25.6 | 31.9 | 29.6 | 31.8 | 24.0 | 18.5 | 30.3 | 29.9 |
| Cond. Cyc'ring | 8.3 | 6.9 | 8.4 | 6.4 | 7.4 | 10.8 | 7.2 | 11.6 | 8.2 | 10.2 | 11.0 | 8.8 |
| Isoparaffins | 5.3 | 7.4 | 5.7 | 8.1 | 6.8 | 4.6 | 5.2 | 3.8 | 5.5 | 2.5 | 3.0 | 3.6 |
| Naphthenes | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Aromatics | 46.6 | 49.1 | 45.8 | 50.5 | 48.9 | 43.2 | 48.3 | 41.8 | 51.1 | 44.6 | 42.3 | 47.0 |
| Monospecifics | 36.9 | 38.5 | 37.5 | 36.3 | 38.7 | 37.1 | 36.8 | 36.0 | 40.8 | 36.4 | 36.1 | 38.7 |
| Dic'ring | 1.7 | 1.9 | 1.5 | 2.0 | 1.8 | 1.1 | 1.9 | 1.2 | 1.7 | 1.6 | 1.4 | 1.4 |
| Tri'ring | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.1 | 0.1 | 0.0 |
| Tetra'ring | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Penta'ring | 0.2 | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 | 0.2 | 0.0 | 0.1 | 0.1 | 0.0 | 0.1 |
| Triphenyls | 0.4 | 0.5 | 0.7 | 0.8 | 0.6 | 0.6 | 0.3 | 0.5 | 0.4 | 0.1 | 0.3 | 0.4 |
| Unidentified | 0.3 | 0.3 | 0.4 | 0.5 | 0.2 | 0.1 | 0.4 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 |
| Total CA, wt. % | 19.1 | 19.9 | 18.0 | 18.4 | 17.7 | 15.0 | 17.1 | 16.6 | 19.1 | 18.1 | 18.3 | 17.3 |
| G.C. Simulated Distillate on, Method D-2887 | | | | | | | | | | | | |
| Weight % Distilled | | | | | | | | Temperature, °F | | | | |
| 0 | -- | -- | 155 | 177 | 136 | 117 | 129 | 129 | 174 | 115 | 115 | 113 |
| 1 | -- | -- | 174 | 209 | 173 | 154 | 156 | 156 | 177 | 151 | 154 | 144 |
| 5 | -- | -- | 215 | 253 | 214 | 212 | 213 | 213 | 241 | 212 | 212 | 194 |
| 10 | -- | -- | 268 | 308 | 267 | 242 | 251 | 253 | 283 | 234 | 234 | 260 |
| 20 | -- | -- | 346 | 376 | 346 | 314 | 332 | 335 | 354 | 296 | 307 | 307 |
| 30 | -- | -- | 406 | 427 | 406 | 376 | 398 | 364 | 409 | 356 | 356 | 368 |
| 40 | -- | -- | 471 | 480 | 470 | 445 | 466 | 418 | 475 | 406 | 407 | 430 |
| 50 | -- | -- | 508 | 513 | 501 | 488 | 499 | 483 | 505 | 477 | 475 | 483 |
| 60 | -- | -- | 549 | 576 | 566 | 543 | 544 | 530 | 569 | 506 | 506 | 531 |
| 70 | -- | -- | 655 | 662 | 647 | 605 | 623 | 593 | 647 | 579 | 574 | 594 |
| 80 | -- | -- | 743 | 747 | 719 | 698 | 736 | 654 | 729 | 674 | 674 | 693 |
| 90 | -- | -- | 890 | 883 | 889 | 840 | 885 | 841 | 884 | 804 | 804 | 830 |
| 95 | -- | -- | 913 | 961 | 978 | 930 | 971 | 931 | 976 | 884 | 884 | 920 |
| 99 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 100 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | 1,008 | -- |

TABLE 8

FIRST HYDROTREATER--MATERIAL BALANCE SUMMARIES

| Run No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Nominal MHSV | 0.6 | 0.6 | 0.6 | 1.2 | 1.2 | 0.6 | 0.6 | 0.6 | 1.2 | 0.6 | 0.6 | 1.2 |
| Temperature, °F | 700 | 666 | 680 | 680 | 700 | 700 | 700 | 730 | 730 | 760 | 760 | 760 |
| Pressure, psig | 1,800 | 1,800 | 2,000 | 2,000 | 2,000 | 2,000 | 1,800 | 1,800 | 1,800 | 1,800 | 2,000 | 2,000 |
| Yield Summary, wt. % | | | | | | | | | | | | |
| Hydrogen | -3.50 | -3.11 | -3.53 | -2.91 | -3.06 | -3.95 | -3.34 | -4.09 | -3.38 | -3.82 | -4.03 | -3.84 |
| Water/gas | 7.25 | 5.71 | 6.40 | 5.67 | 5.48 | 7.50 | 6.69 | 7.34 | 6.95 | 7.54 | 7.55 | 7.50 |
| C1-C4 Gas | 0.41 | 0.66 | 0.64 | 0.67 | 0.24 | 0.60 | 0.21 | 0.76 | 0.83 | 0.72 | 0.69 | 0.89 |
| C5+ Liquid | 95.82 | 96.66 | 96.43 | 96.49 | 97.23 | 95.37 | 96.20 | 95.98 | 95.57 | 95.48 | 95.58 | 95.41 |
| Total | 99.98 | 99.93 | 99.94 | 99.92 | 99.90 | 99.72 | 99.96 | 99.98 | 99.96 | 99.92 | 99.79 | 99.96 |
| Hydrogen, SCFB | 2,378 | 2,109 | 2,396 | 1,978 | 2,073 | 2,683 | 2,267 | 2,778 | 2,293 | 2,591 | 2,732 | 2,605 |
| H ₂ atom gas, SCFB | 537 | 418 | 470 | 415 | 400 | 555 | 508 | 542 | 513 | 558 | 558 | 555 |
| C1-C4 Gas, SCFB | 27 | 41 | 40 | 41 | 15 | 45 | 14 | 43 | 47 | 42 | 41 | 47 |
| Conversion, wt. % | 73.0 | 63.2 | 72.5 | 53.2 | 66.4 | 92.4 | 68.8 | 97.0 | 83.7 | 97.5 | 97.4 | 93.1 |
| Denitrogenation | 85.4 | 95.5 | 96.7 | 96.9 | 97.9 | 99.2 | 96.0 | 98.9 | 96.9 | 97.9 | 99.5 | 98.2 |
| Desulfurization | | | | | | | | | | | | |
| Carbon Balance, % | 93.3 | 96.7 | 96.8 | 98.7 | 95.2 | 96.8 | 96.8 | 95.8 | 91.5 | 94.6 | 93.2 | 95.7 |

TABLE 9

FIRST HYDROTREATER--RUN 8:
GC/MS ANALYSES OF IBP TO 550°F FRACTION

Saturates, wt. percent:

| | |
|-------------------|------|
| Paraffins | 20.4 |
| N'Cond. Cycp'fins | 17.9 |
| Cond. 2-Ring | 14.1 |
| Cond. 3-Ring | 9.0 |
| Isoparaffins | 0.0 |
| Naphthenes | 0.0 |
| Total Saturates | 61.4 |

Aromatics, wt. percent:

| | |
|-----------------|------|
| Mono Species | 27.8 |
| Di " | 5.5 |
| Tri " | 2.6 |
| Tetra " | 0.3 |
| Penta " | 0.1 |
| Thiopheno " | 2.3 |
| Unidentified | 0.0 |
| Total Aromatics | 38.6 |

flash point specifications, will further increase aromatics content beyond the 25 percent maximum allowed in JP-8 fuel.

Therefore, a second hydrotreater is necessary to saturate aromatics to the required level. Addition of a second hydrotreater allows operation of the first at more severe conditions to improve denitrogenation performance. Accordingly, first-stage hydrotreater conditions were recommended based on the best denitrogenation run (Run 12). In Task 3 of this project, operation of the large expanded-bed pilot plant at these conditions made product of the predicted quality.

E. Second Stage Hydrotreating Experiments

In these experiments, effluent from the first hydrotreater was distilled then hydrotreated again in a bench-scale fixed-bed unit to study effects of reaction conditions on aromatics saturation and denitrogenation.

Figure 9 shows the reactor, a heavy-wall tube of type 304 stainless steel, 0.815 inch I.D. by 32 inches long, fitted with a center-mounted 3/16 inch thermowell which is wrapped with electrical heaters to provide five heating zones. A Bran-Lubbe pump controls the oil rate and a Brooks mass flow meter the hydrogen rate. Piping was arranged for downflow of oil and hydrogen, with reactor effluent collected in three high-pressure product receivers. Gas vented from the receivers exits via a scrubber and wet test meter.

Conditions studied ranged from 650 to 760°F reactor temperature at 1,500 and 2,000 psig and weight-hourly space velocities of 0.5 and 1.0. Table 10 shows the feed composition, Table 11 lists conditions and product analyses, and Table 12 summarizes the material balances, closed by adjusting feed input to provide carbon balance.

As discussed in Section IV-A, the purpose of the second hydrotreater is to decrease nitrogen to less than 10 ppm in hydrocracker feed, and to provide the degree of aromatics saturation necessary. Table 11 shows that 2,000 psig and 700°F satisfied denitrogenation requirements and maximized aromatics saturation. However, 2,000 psig at 760°F was recommended for the design basis because this further lowered nitrogen in the product, enhancing hydrocracker catalyst life and performance. This recognizes that additional aromatics saturation will take place in the hydrocracker to meet jet fuel specifications.

A run at the recommended conditions yielded about ten gallons of product similar to the product from Run 9 described in Table 11. Distillation yielded about 35 weight percent of 550°F+ material for the hydrocracking study discussed in Section IV-F.

F. Hydrocracking Experiments

Two units were used in these runs, the second hydrotreater described in Section IV-E, and a smaller unit with the reactor cooled by a molten salt bath. Table 4 shows composition of the hydrocracking catalyst used in both units. Stabilized reactor operation could not be achieved during the experiments in the first unit, however, using the high-nitrogen feed. The second unit was fed only with low-nitrogen (less than 10 ppm) material and performed well.

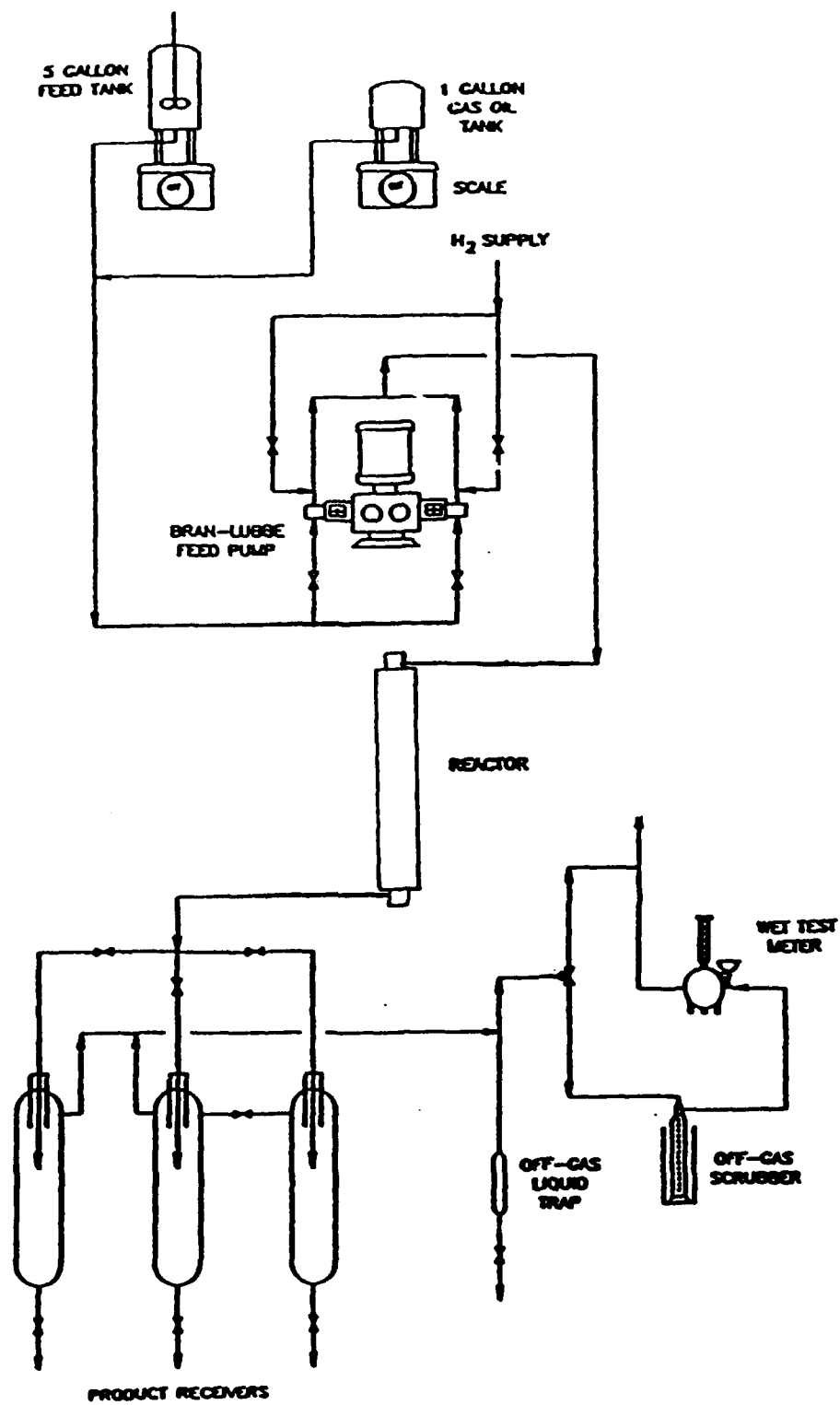


FIGURE 9
HYDROTREATING PILOT PLAN--SECOND HYDROTREATER

TABLE 10

SECOND HYDROTREATER--FEEDSTOCK ANALYSES

Elemental Analysis, Dry Basis:

| | |
|------------------|-------|
| Carbon, wt.% | 87.79 |
| Hydrogen, wt.% | 12.49 |
| Nitrogen, ppm | 120 |
| Sulfur, ppm | 270 |
| Oxygen, ppm | 1,000 |
| Atomic H/C Ratio | 1.70 |
| API Gravity | 29.6 |
| Specific Gravity | 0.879 |

Mass Spectral Results, wt.%

| | |
|------------------|------|
| Saturates | 65.3 |
| Paraffins | 9.6 |
| NCond. Cycp'fins | 29.1 |
| Cond. 2-Ring " | 18.5 |
| Cond. 3-Ring " | 8.2 |
| Isoparaffins | 0.0 |
| Naphthenes | 0.0 |
| Aromatics | 34.7 |
| Mono Species | 29.6 |
| Di " | 3.6 |
| Tri " | 0.8 |
| Tetra " | 0.1 |
| Penta " | 0.0 |
| Thiopheno " | 0.6 |
| Unidentified | 0.0 |
| Total CA, wt.% | 12.9 |

G.C. Simulated Distillation, Method D-2887

| Wt. % Distilled | Temperature, F |
|-----------------|----------------|
| 0 | 172 |
| 1 | 179 |
| 5 | 241 |
| 10 | 279 |
| 20 | 350 |
| 30 | 395 |
| 40 | 439 |
| 50 | 479 |
| 60 | 521 |
| 70 | 574 |
| 80 | 632 |
| 90 | 729 |
| 95 | 792 |
| 99 | 901 |
| 100 | 939 |

| Run No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| WHSV | 0.5 | 0.5 | 1.0 | 1.0 | 1.0 | 1.0 | 0.5 | 0.5 | 1.0 |
| Temperature, F | 700 | 760 | 760 | 760 | 700 | 650 | 650 | 650 | 760 |
| Pressure, psig | 2,000 | 2,000 | 2,000 | 1,500 | 1,500 | 1,500 | 1,500 | 2,000 | 2,000 |

Elemental Analysis, Dry Basis:

| Carbon, wt. % | 84.17 | 86.95 | 87.02 | 87.42 | 87.22 | 87.60 | 87.69 | 87.65 |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Hydrogen, wt. % | 13.06 | 13.41 | 13.06 | 12.64 | 12.72 | 12.42 | 12.66 | 12.77 |
| Nitrogen, ppm | 1 | 2 | 1 | 4 | 6 | 29 | 18 | 4 |
| Sulfur, ppm | 16 | 11 | 16 | 27 | 25 | 21 | 15 | 12 |
| Oxygen, ppm | 200 | 200 | 200 | 200 | 300 | 300 | 200 | 200 |
| Atomic H/C Ratio | 1.85 | 1.84 | 1.79 | 1.72 | 1.74 | 1.69 | 1.72 | 1.74 |
| API Gravity | 33.7 | 33.1 | 33.2 | 31.5 | 31.2 | 29.7 | 30.6 | 31.6 |
| Specific Gravity | 0.857 | 0.849 | 0.859 | 0.868 | 0.870 | 0.878 | 0.873 | 0.867 |

Mass Spectral Results, wt. %

| Compound | 70.2 | 72.4 | 63.1 | 68.5 | 77.9 | 73.6 |
|---------------------|------|-------|------|-------|-------|------|
| Saturates | | | | | | |
| Paraffins | 81.1 | 70.2 | 72.4 | 63.1 | 68.5 | 77.9 |
| NCond. Cycp'ins | 9.4 | 9.4 | 9.1 | 8.9 | 7.5 | 7.3 |
| Cond. 2-Ring " | 35.8 | 32.0 | 32.3 | 31.0 | 33.2 | 34.8 |
| Cond. 3-Ring " | 27.3 | 22.2 | 23.2 | 17.6 | 21.4 | 22.6 |
| Isoparaffins | 8.7 | 6.5 | 7.8 | 5.6 | 6.4 | 6.9 |
| Naphthenes | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Aromatics | | | | | | |
| Mono Species | 18.9 | 29.8 | 27.6 | 36.9 | 31.5 | 26.4 |
| Di | 16.6 | 24.9 | 24.8 | 33.3 | 28.3 | 23.2 |
| Tri | 1.4 | 3.4 | 1.6 | 1.1 | 1.7 | 2.0 |
| Tetra | 0.7 | 0.9 | 0.7 | 0.5 | 0.7 | 0.9 |
| Penta | 0.1 | 0.3 | 0.1 | 0.0 | 0.0 | 0.1 |
| Thiopheno | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | 0.0 | 0.3 | 0.3 | 0.6 | 0.8 | 0.2 |
| Unidentified | | | | | | |
| Total CA, Wt. % | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | 4.37 | 11.19 | 9.40 | 12.66 | 10.64 | 9.27 |

G.C. Simulated Distillation, Method D-2887

[illegible]

TABLE 12

SECOND HYDROTREATER--MATERIAL BALANCE SUMMARIES

| Run No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|-------|
| WHSV | 0.5 | 0.5 | 1.0 | 1.0 | 1.0 | 1.0 | 0.5 | 0.5 | 1.0 |
| Temperature, F | 700 | 760 | 760 | 760 | 700 | 650 | 650 | 650 | 760 |
| Pressure, psig | 2,000 | 2,000 | 2,000 | 1,500 | 1,500 | 1,500 | 1,500 | 2,000 | 2,000 |
| Yield Summary, wt. % | | | | | | | | | |
| Hydrogen | -1.27 | -1.21 | -0.84 | -0.36 | -0.46 | -0.08 | -0.32 | -0.67 | -0.48 |
| Heteroatom Gas | 0.13 | 0.13 | 0.13 | 0.13 | 0.12 | 0.12 | 0.13 | 0.13 | 0.13 |
| C1 - C ₄ Gas | 1.30 | 1.63 | 1.45 | 1.43 | 1.27 | 0.66 | 1.13 | 1.41 | 1.55 |
| C5+ Liquid | 103.08 | 99.49 | 99.59 | 99.15 | 99.51 | 99.67 | 99.12 | 99.47 | 98.78 |
| Total | 103.25 | 100.04 | 100.33 | 100.34 | 100.45 | 100.37 | 100.06 | 100.34 | 99.99 |
| Hydrogen, SCFB | 734 | 702 | 486 | 209 | 264 | 44 | 188 | 386 | 276 |
| H ₂ atom gas, SCFB | 8 | 8 | 8 | 8 | 7 | 7 | 8 | 8 | 8 |
| C1-C ₄ Gas, SCFB | 56 | 72 | 66 | 64 | 56 | 26 | 48 | 60 | 74 |
| Conversion, wt. % | | | | | | | | | |
| Denitrogenation | 99.1 | 98.3 | 99.2 | 96.7 | 95.0 | 76.1 | 85.2 | 86.8 | 96.7 |
| Desulfurization | 93.9 | 96.0 | 94.1 | 90.1 | 90.8 | 92.3 | 94.5 | 96.7 | 95.6 |
| Carbon Balance, % | 90.9 | 78.9 | 90.2 | 99.6 | 99.5 | 99.6 | 95.4 | 99.6 | 97.7 |

Rapid catalyst deactivation occurred in the first unit when feeding once-hydrotreated 550°F+ tar oil containing 250 to 300 ppm nitrogen. Presumably, nitrogen-containing materials peculiar to coal-derived liquids had poisoned active sites in the catalyst, requiring increasingly higher reactor temperatures to effect conversion.

Organic nitrogen compounds are thought to act as permanent catalyst poisons in petroleum hydrocracking, but the ammonia produced by reaction of organic nitrogen does not affect the catalyst permanently (5). For coal-derived liquids, nitrogen conversion to ammonia may occur more slowly than for petroleum-derived stocks, thus accounting for a greater degree of catalyst deactivation. More study is necessary to verify and determine the cause of this apparent difference in hydrocracking performance of petroleum and coal-derived liquids.

Several short scoping runs were completed in the second unit. With twice-hydrotreated feed containing about 5 ppm nitrogen, about 70 percent of the 550°F+ material was converted to lower boiling 550°F minus material. This provided the recommended design basis for hydrocracker conditions: 650°F, 1,600 psig, and 0.7 space velocity. Good catalyst performance in these runs was attributed to low nitrogen content of the feed.

The recommended hydrocracker conditions were further confirmed in the Task 3 work described later. In particular, the effects of hydrocracker recycle on product quality are discussed.

G. Production of Jet Fuel Samples

Because of the difficulties met in developing viable hydrocracker conditions, there was not sufficient good quality hydrocracked material available to blend into the small samples in Task 2. However, hydrocracked material was included in the large sample of JP-8 produced in Task 3 of this project.

Table 13 shows how small samples of JP-4, JP-8, and JP-8X were prepared by blending distillation cuts of hydrotreated tar oil. Distillation results shown in Figures 10 through 12 confirm that the blended fuels meet boiling range specifications. Tables 14 and 15 compare the remaining inspection results against specifications for the respective fuels. Note that several analyses which require large aliquots of fuel could not be run because of limited sample quantity.

The JP-4 product met all specifications for which analyses were performed except for copper strip corrosion and heating value. The JP-8 and JP-8X products failed copper strip corrosion, existent gum, and flash point specifications. However, as specified by the client (USAF), none of these samples was clay-treated or treated with specified antioxidant additives, which may explain failure to pass the copper strip corrosion and gum content tests. Inclusion of too much material boiling in the IBP to 300°F range may explain the slightly low JP-4 heating value and the failure of JP-8 to meet the flash point specification.

TABLE 13

Blending for Jet Fuel Products

| Cut No. ----- | Boiling Range, F ----- | Weight, gms. ----- | | |
|-------------------|------------------------------|-----------------------|---------------|----------------|
| | | JP-4 ----- | JP-8 ----- | JP-8X ----- |
| 1 | IBP-300 | 3,886 | 2,862 | -- |
| 2 | 300-375 | 26 | 5,421 | 1,797 |
| 3 | 375-400 | -- | -- | 5,323 |
| 4 | 400-475 | 1,304 | 6,006 | 2,932 |
| 5 | 475-520 | -- | -- | 1,113 |
| 6 | 520-575 | -- | -- | 3,123 |
| Total | | 5,213 | 14,289 | 14,288 |
| Est. Volume, gal. | | 1.7 | 4.6 | 4.4 |

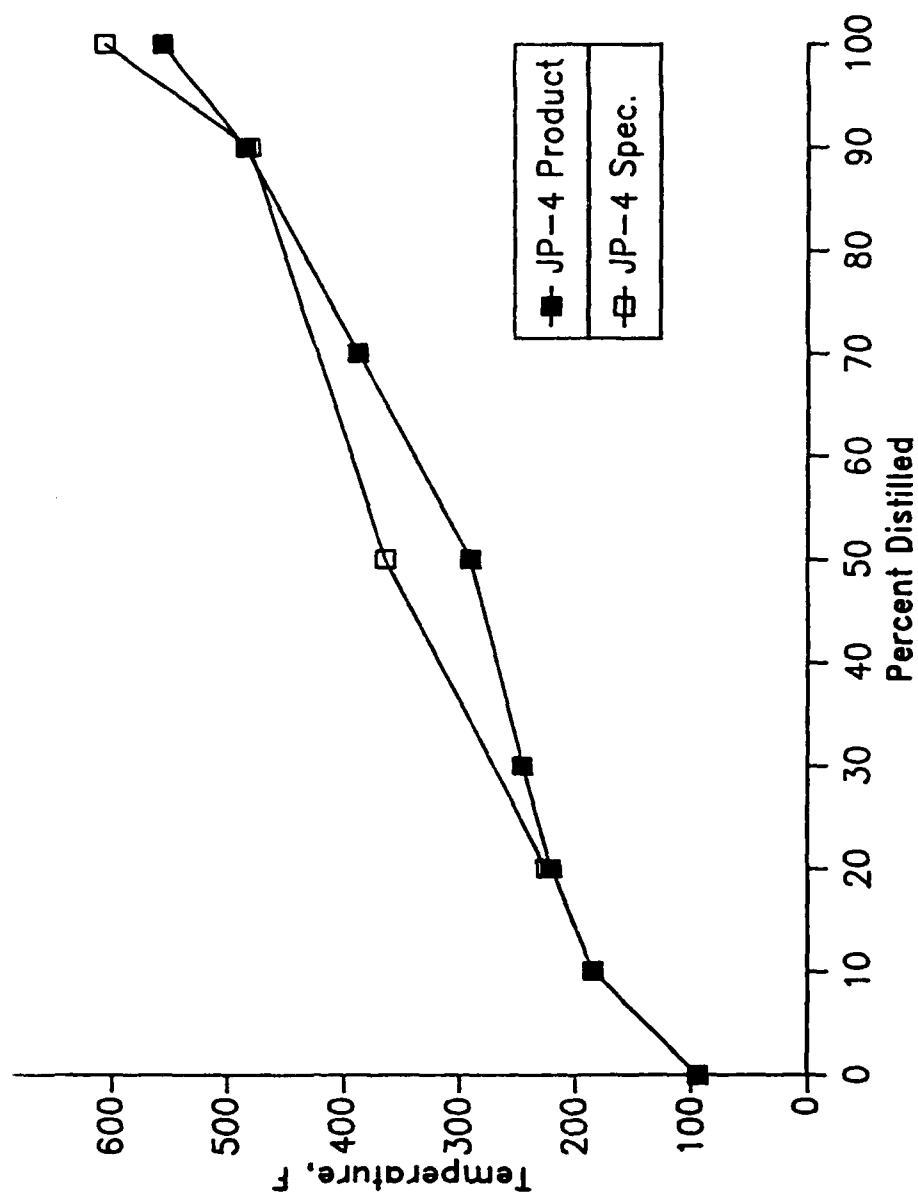


FIGURE 10
BOILING RANGE OF JP-4 PRODUCT COMPARED TO SPECIFICATION

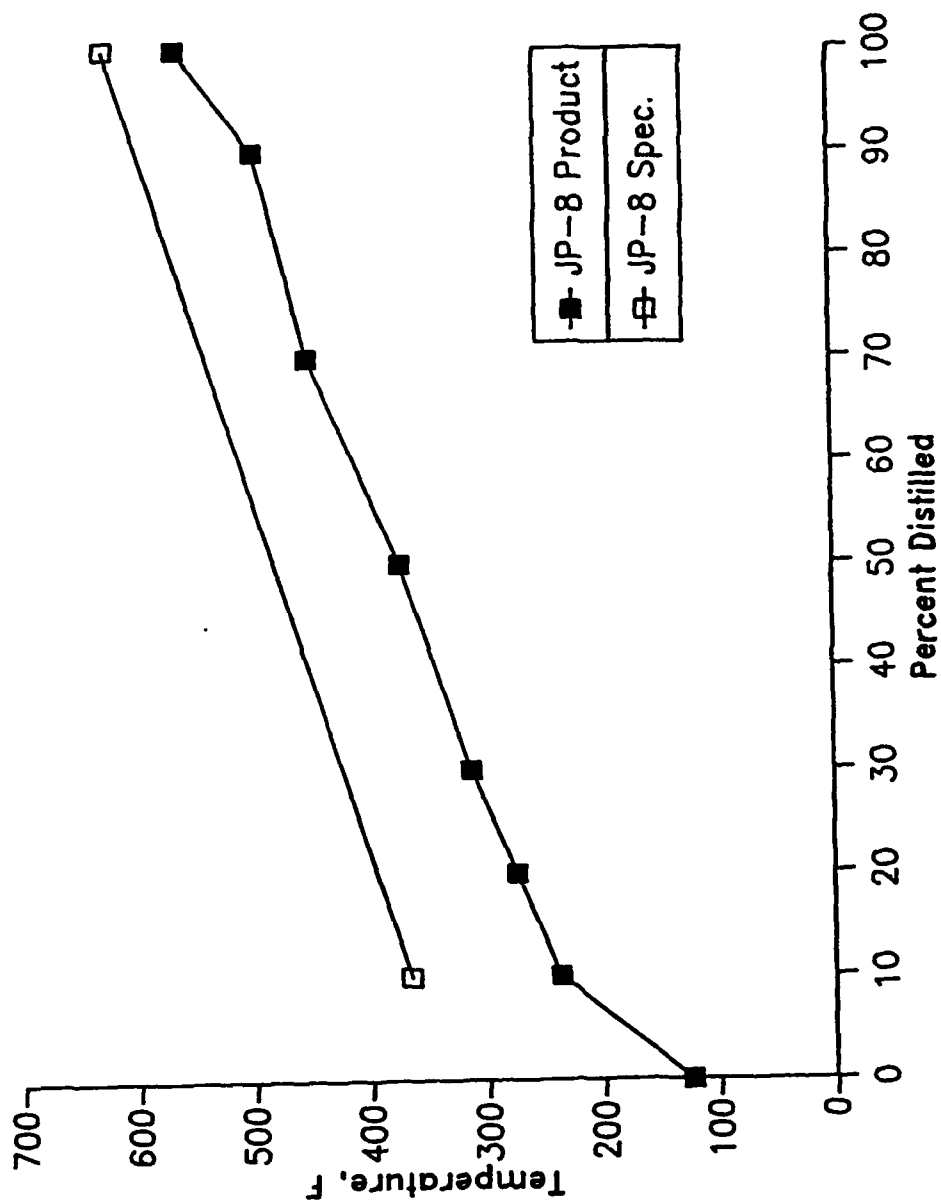


FIGURE 11
BOILING RANGE OF JP-8 PRODUCT COMPARED TO SPECIFICATION

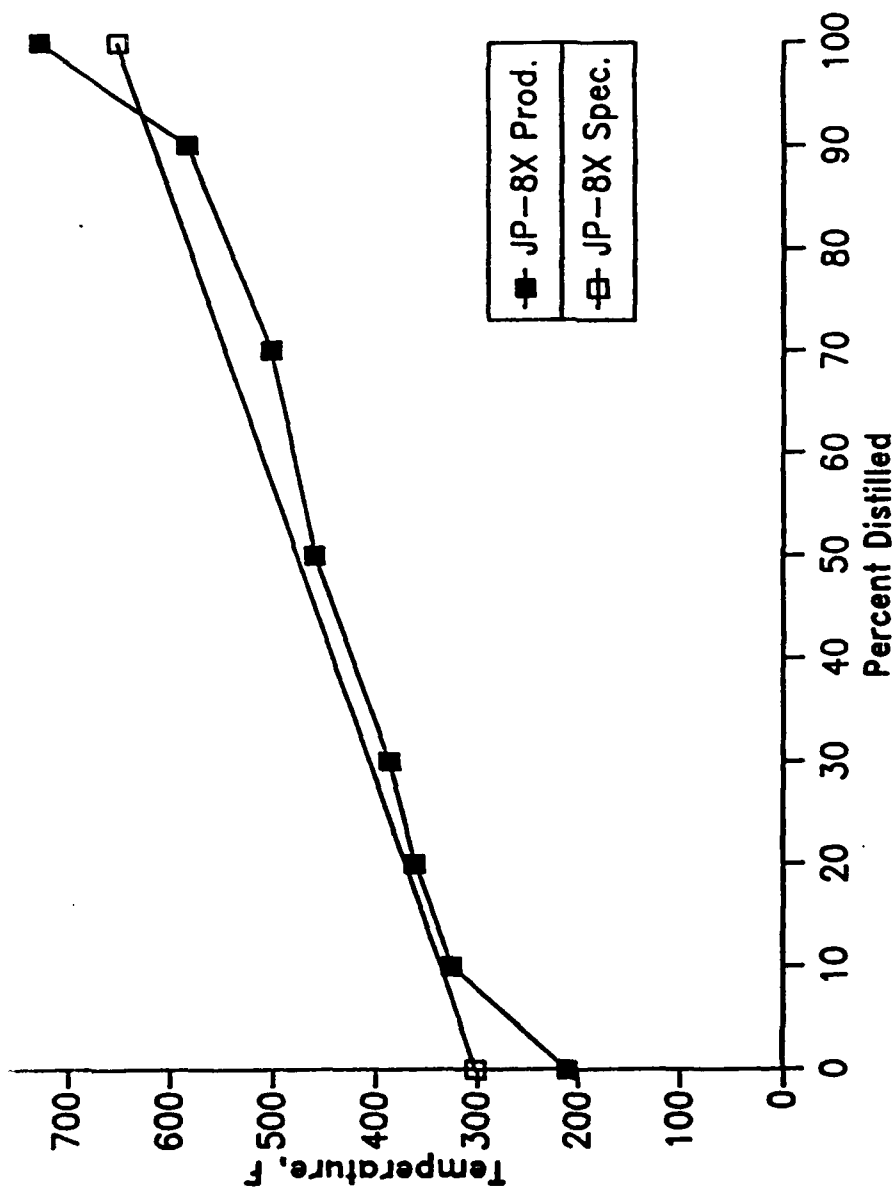


FIGURE 12
BOILING RANGE OF JP-8X PRODUCT COMPARED TO SPECIFICATION

TABLE 14

INSPECTIONS OF JP-4 PRODUCT

| <u>Requirements</u> | <u>JP-4 Specification</u> | <u>JP-4 Inspection</u> |
|--|-------------------------------|----------------------------|
| Color, Saybolt | Report | |
| Total acid number, mg KOH/g, max. | 0.015 | 0.00 |
| Aromatics, vol %, max. | 25.0 | 10.0 |
| Olefins, vol % max. | 5.0 | 2.0 |
| Mercaptan sulfur, wt.% max. | 0.002 | 0.0001 |
| Sulfur, total wt.% max. | 0.40 | 0.002 |
| Distillation temperatures, C | | |
| Initial boiling point | Report | 87.2 |
| 10 percent recovered, max. | Report | 105 |
| 20 percent recovered, max. | 145 | 111 |
| 50 percent recovered, max. | 190 | 128 |
| 90 percent recovered, max. | 245 | 221 |
| End Point, max. | 270 | 253 |
| Residue, vol %, max | 1.5 | |
| Loss, vol %, max | 1.5 | 1.5 |
| Flash Point, C | No spec | |
| Density, kg/l, min. at 15 C | 0.751 | |
| Density, kg/l, max. at 15 C | 0.802 | |
| Vapor Pressure, 37.8 C, kPa | 14 to 21 | 15.9 |
| Freezing Point, C, max. | -58 | -79 |
| Viscosity, at -20 C, c'stokes max | No spec | 0.9 @ 38 C |
| Heating value, Aniline--gravity product, min, | 5,250 | 4,965 |
| Hydrogen content, wt.%, min. | 13.6 | |
| or Smoke Point, mm, min. | 20.0 | 30 |
| Copper strip corrosion, 2 hr at 100 C, max. | 1b | 2.3 |
| Thermal stability: Change in pressure drop, mm of Hg., max. | 25 | |
| Preheater deposit code, less than | 3 | |
| Existent gum, mg/100 ml, max | 7.0 | 1.8 |
| Particulate matter, mg/liter, max | 1.0 | |
| Filtration time, minutes, max | 10 | |
| Water Separometer Index, modified, min. | 85 | 79 |
| Fuel System icing inhibitor, vol.% | 0.10-0.15 | |
| Electrical conductivity, CU | 200-600 | |
| Cetane Index | No spec | |
| Peroxide number, wt. ppm, max. | No spec | |

TABLE 15

INSPECTION OF JP-8 AND JP-8X PRODUCTS

| <u>Requirements</u> | <u>JP-8 Specification</u> | <u>JP-8 Inspection</u> | <u>JP-8X Inspection</u> |
|---------------------------------------|-------------------------------|----------------------------|-----------------------------|
| Color, Saybolt | Report | 30 | |
| Total Acid Number, mg KOH/gm, max. | 0.015 | 0.00 | 0.00 |
| Aromatics, Vol%, max. | 25.0 | 16.5 | 19.0 |
| Olefins, Vol%, max. | 5.0 | 3.0 | 4.0 |
| Sulfur, Mercaptan, Wt%, max. | 0.001 | 0.001 | 0.0001 |
| Sulfur, Total, Wt%, max. | 0.4 | 0.002 | 0.002 |
| Distillation Temperature, °C | | | |
| Initial Boiling Point | Report | 105 | 184°C |
| 10% Recovered, max. | 186 | 137 | 187 |
| 20% Recovered, max. | Report | 151 | 193 |
| 50% Recovered, max. | Report | 193 | 211 |
| 90% Recovered, max. | Report | 256 | 268 |
| End Point, max. | 330 | 268 | 291°C |
| Residue, Vol%, max. | 1.5 | | |
| Loss, Vol%, max. | 1.5 | 2.3 | 2.5 |
| Flash Point, °C, max. | 38 (100) | 26 | 35 |
| Gravity, °API or | 37-51 | 37.3 | 32.7 |
| Density, kg/m ³ at 15°C | 775-840 | 838 | 862 |
| Freezing Point, °C, max. | -50 | -56 | -45 |
| Viscosity at -20°C, C'stokes, max. | 8.0 (8.0) | | 1.8@100°F |
| Net Heat of Combustion, MJ/kg min. | 42.8 | | |
| Combustion: | | | |
| (1) Hydrogen Content, wt% min., | 13.6 | | |
| or (2) Smoke Point, mm min. | 25 | | |
| (3) Smoke point, mm min. and | 20 | | |
| Napthalenes, Vol% max. | 3.0 | 0.36 | 0.56 |
| Copper Strip Corrosion, | NDT 1b | 2.3 | |
| 2 Hr @ 100°C (212°F) | | | |
| Thermal Stability: | | | |
| Change in Pressure Drop, mm Hg max. | 25 | 0 | 0 |
| Heater Tube Deposit Visual Rating | Less than Code 3 | -1 | -1 |
| Existent Gum, mg/100 ml, max. | 7.0 | 13.4 | 15.0 |
| Particulate Matter, mg/Liter, max. | 1.0 | | |
| Water Separation Index, Modified min. | 70 | 75 | 70 |
| Fuel System Icing Inhibitor, Vol% | 0.1-0.15 | | |

SECTION V

TASK 3 RESULTS

As outlined in Section II, the objectives of Task 3 are to carry out pilot plant testing to confirm the process design, and provide barrel quantities of product for testing by the Air Force. The technical approach consists of two stages of hydrotreating followed by distillation and hydrocracking of the higher boiling fractions to yield JP-8 jet fuel as outlined in the process flow diagram, Figure 4.

A. First-Stage Hydrotreating

As discussed in Section IV-C, expanded-bed reactors will be necessary for temperature control in the hydrotreaters for commercial tar oil processing. Because Amoco's expanded-bed pilot plant was unavailable within the required project schedule, Amoco requested that Lummus Crest Incorporated (LCI) perform the hydrotreating work. LCI maintains an expanded-bed pilot plant of appropriate size for this operation as part of their LC-Fining (tm) process studies.

LCI completed the hydrotreating operations at conditions specified by Amoco, based on the bench scale experiments discussed in Section IV-D of this report. Appendix A presents LCI's report on the hydrotreating operations, including a brief description of the unit.

Amoco distilled the hydrotreated product (excluding that collected during an upset condition at LCI) to remove water and other materials boiling below 300°F. Table 16 shows analyses of this 300°F+ hydrotreated tar oil, used as feed to the second hydrotreater.

B. Second-Stage Hydrotreating

Second-stage hydrotreating was completed in Amoco's pilot plant, shown schematically in Figure 13. The unit features two thirteen-foot long reactors with multiple heating zones, four hydrogen quench points, and travelling thermocouples in each reactor. Bran-Lubbe pumps control the oil feed rate and Brooks mass flow meters the hydrogen rates. The piping was arranged for downflow of oil and hydrogen through the first reactor only, bypassing the second reactor, with the effluent passing on level control to a product receiver via a high pressure gas-liquid separator. Gas vented from the separator and receiver exits through a scrubber and wet test meter.

The reactor was controlled at the conditions recommended in Section IV-E, 760°F, 2,000 psig, and 1.0 WHSV, except that throughput was increased to about 1.5 WHSV for most of the run to expedite sample production. Table 4 shows the catalyst composition, the same as for the bench-scale experiments. Table 17, a typical control analysis, shows that product quality is similar to bench-scale runs at similar conditions, specifically, Runs 3 and 9 in Table 11. Elemental analyses and material balances were not routinely performed during this production run.

The product was distilled to yield light ends, a 160 to 550°F heartcut, and 550°F+ material for hydrocracker feed. The respective yields were 0.2, 71.4, and 28.4 weight percent. Table 18 shows compositions of the heartcut and hydrocracker feed fractions.

TABLE 16

SECOND HYDROTREATER--TYPICAL FEED PROPERTIES

Elemental Analysis, Dry Basis

| | |
|---------------|-------|
| Carbon, wt% | 87.79 |
| Hydrogen, wt% | 12.49 |
| Nitrogen, ppm | 120 |
| Sulfur, ppm | 270 |
| Oxygen, ppm | 1000 |

| | |
|------------------|------|
| Atomic H/C Ratio | 1.70 |
|------------------|------|

| | |
|------------------|-------|
| API Gravity | 29.6 |
| Specific Gravity | 0.879 |

Mass Spectral Results, wt%

| | |
|-------------------|------|
| Saturates | 65.3 |
| Paraffins | 9.6 |
| NCond. Cycp' fins | 29.1 |
| Cond. 2-Ring fins | 18.5 |
| Cond. 3-Ring fins | 8.2 |

| | |
|-------------------|------|
| Aromatics | 34.7 |
| Mono Species | 29.6 |
| Di Species | 3.6 |
| Tri Species | 0.8 |
| Tetra Species | 0.1 |
| Penta Species | 0.0 |
| Thiopheno Species | 0.6 |

| | |
|---------------|------|
| Unidentified | 0.0 |
| Total CA, wt% | 12.9 |

G. C. Simulated Distillation, Method D-2887

| <u>Wt% Distilled</u> | <u>Temperature, °F</u> |
|----------------------|------------------------|
| 0 | 172 |
| 1 | 179 |
| 5 | 241 |
| 10 | 279 |
| 20 | 350 |
| 30 | 395 |
| 40 | 439 |
| 50 | 479 |
| 60 | 521 |
| 70 | 574 |
| 80 | 632 |
| 90 | 729 |
| 95 | 792 |
| 99 | 901 |
| 100 | 939 |

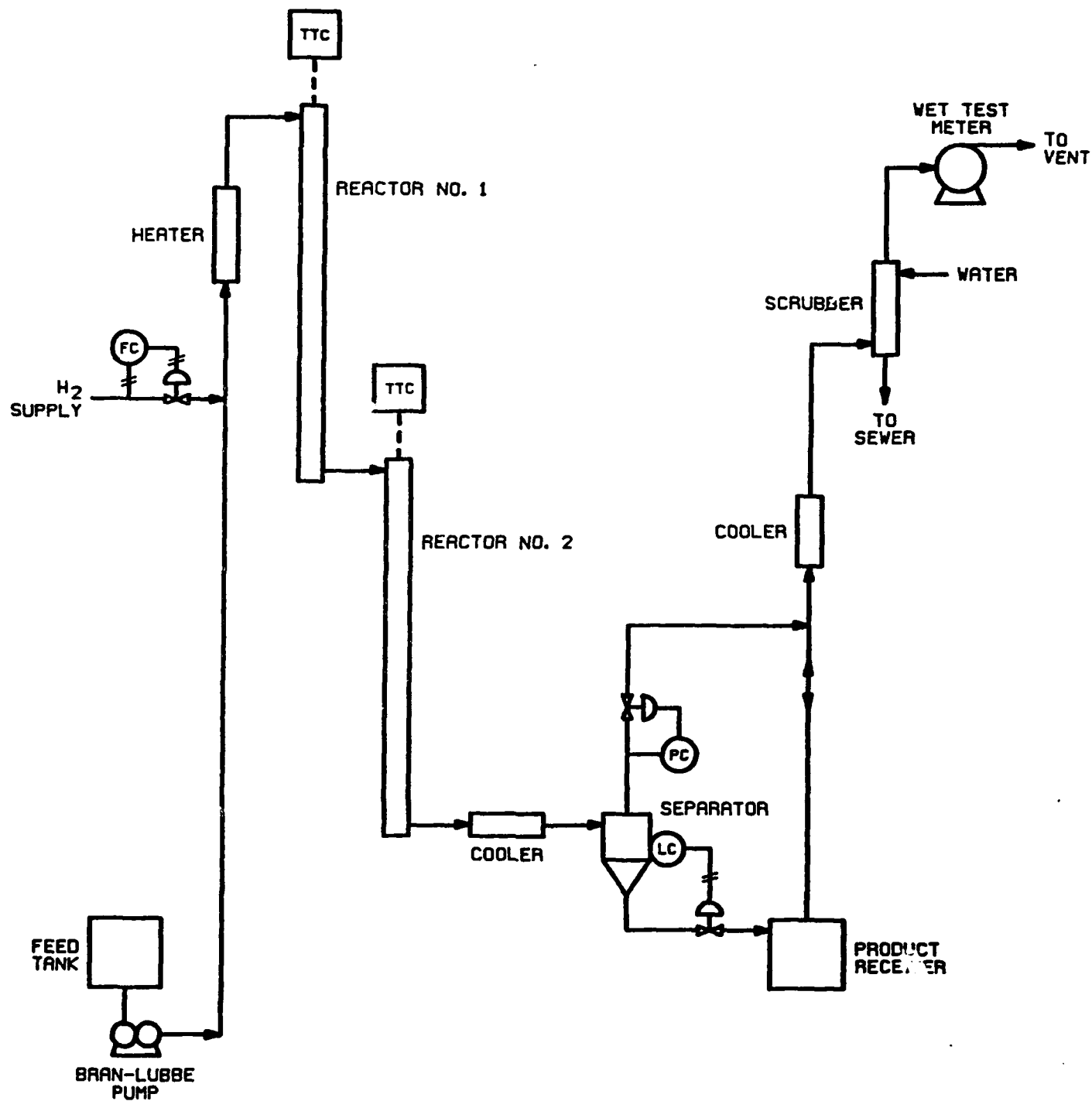


FIGURE 13
HYDROTREATING/HYDROCRACKING PILOT PLANT

TABLE 17

SECOND HYDROTREATER--TYPICAL PRODUCT ANALYSESMass Spectral Results, Wt%

| | |
|-----------------------------|------|
| Saturates | 72.6 |
| Paraffins | 9.0 |
| NCond. Cycloparaffins | 33.4 |
| Cond. 2-Ring Cycloparaffins | 22.9 |
| Cond. 3-Ring Cycloparaffins | 7.3 |
| Aromatics | 27.4 |
| Mono Species | 24.3 |
| Di Species | 1.8 |
| Tri Species | 0.8 |
| Tetra Species | 0.3 |
| Penta Species | 0.0 |
| Thiopheno Species | 0.3 |
| Unidentified | 0.0 |
| Total CA, Wt% | 9.9 |

GC Simulated Distillation, Method D-2887

| Wt% Distilled | Temperature, °F |
|---------------|-----------------|
| 0 | 135 |
| 1 | 169 |
| 5 | 214 |
| 10 | 261 |
| 20 | 331 |
| 30 | 378 |
| 40 | 433 |
| 50 | 481 |
| 60 | 511 |
| 70 | 570 |
| 80 | 658 |
| 90 | 774 |
| 95 | 881 |
| 99 | 1,005 |
| 100 | 1,018 |

C. Hydrocracking

Hydrocracking was carried out in the second reactor of the pilot plant shown in Figure 13, over catalyst diluted 50 percent by volume with non-porous alumina chips to aid heat dissipation. Table 4 shows the catalyst composition, the same as for the bench-scale experiments discussed in Section IV-F.

Hydrotreated 550°F+ material was fed to the hydrocracker, initially at the conditions suggested by the bench-scale experiments, 650°F, 1,600 psig, and 0.7 WHSV. However, it was necessary to increase temperature to 670°F to achieve the targeted 70 percent conversion of 550°F+ to lower boiling materials. After hydrocracking about half of the available 550°F+ material, the unit was temporarily shut down and the product distilled to provide 550°F+ hydrocrackate for a recycle experiment.

During feed blending for the recycle run, a malfunctioning relief valve resulted in losses of hydrotreated 550°F+ material. As a result, feed for the recycle run contained about 45 percent of the hydrocracked 550°F material instead of 29 percent as implied by material balances in Section IV-A of this report. Therefore, the effects of recycle shown by these results, while directionally correct, may be amplified somewhat.

Tables 19 and 20 show the effects of recycle on product quality and yields. Although only slightly higher temperature (674 vs. 670°F) was required for 70 percent conversion with recycle, gases and light liquid yields increased dramatically. Table 20 shows that gas production more than doubled and that fifty percent more light liquid was produced in the recycle case, at the expense of desirable heartcut material.

However, with recycle the feed contained about ten percent more saturates, mostly paraffinic, that might be expected to increase gas yields in hydrocracking. In an optimized process a heavier heartcut might be taken downstream of the hydrotreaters and the conversion per pass decreased in the hydrocracker to improve liquid yields at the expense of gas makers. However, these represent minor operational rather than design changes to the process and will not significantly affect equipment sizing in Task 4.

These results confirm the recommended design basis by showing the viability of extensive recycle in the hydrocracker, albeit at higher than design concentration. The lower hydrocracker temperature (650°F) recommended in the design basis remains preferred over the 670 to 674°F used in these runs, because this will decrease severity and improve liquid yields.

D. Jet Fuel Production--Blending, Clay Treating, and Inspection

Table 21 shows the inspection analyses of the two jet fuel samples that were produced, designated JP-8 HC and JP-8 HT. The JP-8HC fuel contains heartcuts of hydrotreated and hydrocracked stocks, blended according to the design basis in Section IV-A. HT fuel contains only hydrotreated stock, because there was not enough hydrocrackate for blending because of the losses during the recycle run discussed in Section V-C.

TABLE 18

SECOND HYDROTREATER--ANALYSES OF PRODUCT FRACTIONS

| <u>Elemental Analysis, Dry Basis</u> | <u>Heartcut 160-550°F</u> | <u>Hydrocracker Feed 550°F+</u> |
|---|-------------------------------|-------------------------------------|
| Carbon, wt% | 86.91 | 87.49 |
| Hydrogen, wt% | 12.75 | 12.31 |
| Nitrogen, ppm | 3 | 8 |
| Sulfur, ppm | | 26 |
| Atomic H/C Ratio | | 1.68 |
| API Gravity | 35.0 | 24.5 |
| Specific Gravity | 0.850 | 0.907 |
| <u>Mass Spectral Results, wt%</u> | | |
| Saturates | 76.0 | 66.3 |
| Paraffins | 8.5 | 20.7 |
| NCond. Cycloparaffins | 34.9 | 17.6 |
| Cond. 2-Ring Cycloparaffins | 26.6 | 16.0 |
| Cond. 3-Ring Cycloparaffins | 6.0 | 11.9 |
| Aromatics | 24.0 | 33.7 |
| Mono Species | 23.0 | 21.2 |
| Di Species | 0.81 | 6.1 |
| Tri Species | 0.00 | 3.3 |
| Tetra Species | 0.00 | 0.7 |
| Penta Species | 0.00 | 0.1 |
| Thiopheno Species | 0.03 | 2.1 |
| Unidentified | 0.00 | 0.2 |
| Total CA, wt% | 12.5 | 14.2 |
| <u>GC Simulated Distillation, Method D-2887</u> | | |
| <u>wt% Distilled</u> | | |
| 0 | 173 | 488 |
| 1 | 175 | 500 |
| 5 | 217 | 564 |
| 10 | 250 | 590 |
| 20 | 302 | 651 |
| 30 | 349 | 690 |
| 40 | 380 | 730 |
| 50 | 416 | 788 |
| 60 | 466 | 845 |
| 70 | 487 | 889 |
| 80 | 507 | 927 |
| 90 | 560 | 993 |
| 95 | 586 | -- |
| 99 | 658 | -- |
| 100 | 674 | -- |

TABLE 19

HYDROCRACKER--EFFECT OF RECYCLE

| | <u>Without Recycle</u> | | <u>With Recycle*</u> | |
|---|------------------------|----------------|----------------------|----------------|
| | <u>Feed</u> | <u>Product</u> | <u>Feed</u> | <u>Product</u> |
| Carbon, wt% | 87.49 | 86.20 | 87.10 | 85.97 |
| Hydrogen, wt% | 12.31 | 13.93 | 12.78 | 14.09 |
| Nitrogen, ppm | 8 | | | 1 |
| Sulfur, ppm | 26 | 2 | 35 | <1 |
| Atomic H/C Ratio | 1.68 | 1.92 | 1.75 | 1.95 |
| API Gravity | 24.5 | | | |
| Specific Gravity | 0.907 | 0.828 | 0.894 | 0.793 |
| <u>Mass Spectral Results, wt%</u> | | | | |
| Saturates | 66.3 | 85.7 | 73.6 | 90.1 |
| Paraffins | 20.7 | 27.4 | 34.4 | 45.3 |
| NCond. Cycloparaffins | 17.6 | 33.8 | 15.6 | 32.5 |
| Cond. 2-Ring Cycloparaffins | 16.0 | 15.0 | 12.0 | 7.8 |
| Cond. 3-Ring Cycloparaffins | 11.9 | 9.5 | 11.5 | 4.5 |
| Aromatics | 33.7 | 14.3 | 26.4 | 9.9 |
| Mono Species | 21.2 | 13.1 | 14.4 | 0.0 |
| Di Species | 6.1 | 0.0 | 5.0 | 0.0 |
| Tri Species | 3.3 | 0.8 | 3.5 | 0.0 |
| Tetra Species | 0.7 | 0.1 | 1.0 | 0.0 |
| Penta Species | 0.1 | 0.0 | 0.2 | 0.0 |
| Thiopheno Species | 2.1 | 0.2 | 2.3 | 0.0 |
| Unidentified | 0.2 | 0.0 | 0.0 | 0.0 |
| Total CA, wt% | 14.2 | 4.5 | 11.6 | 5.3 |
| <u>GC Simulated Distillation, Method D-2887</u> | | | | |
| <u>wt% Distilled</u> | | | | |
| 0 | 488 | 91 | 485 | 76 |
| 1 | 500 | 114 | 495 | 79 |
| 5 | 564 | 191 | 550 | 129 |
| 10 | 590 | 226 | 577 | 187 |
| 20 | 651 | 290 | 633 | 234 |
| 30 | 690 | 359 | 674 | 279 |
| 40 | 730 | 433 | 705 | 331 |
| 50 | 788 | 500 | 739 | 399 |
| 60 | 845 | 588 | 793 | 506 |
| 70 | 889 | 691 | 851 | 674 |
| 80 | 927 | 809 | 900 | 786 |
| 90 | 993 | 912 | 960 | 900 |
| 95 | -- | 976 | 1,017 | 969 |
| 99 | -- | -- | -- | -- |
| 100 | -- | -- | -- | -- |

*Feed contains 45% hydrocracked 550°F+ material.

TABLE 20

EFFECT OF RECYCLE ON HYDROCRACKER YIELD

| | <u>Without Recycle</u> | <u>With Recycle</u> |
|-----------------------------|------------------------|---------------------|
| Nominal WHSV | 0.7 | 0.7 |
| Temperature, °F | 670 | 674 |
| Pressure, psig | 1,600 | 1,600 |
| 550°F+ Conversion, % | 70.1 | 70.3 |
| Hydrogen, SCFB | 1,165 | 1,289 |
| Reactor Effluent, % of Feed | | |
| C1 | 0.006 | 0.004 |
| C2 | 0.065 | 0.053 |
| C3 | 0.485 | 0.526 |
| C4 | 1.41 | 3.80 |
| C5 | 1.51 | 4.94 |
| C6-210°F | 8.21 | 12.9 |
| 210-550°F | 65.3 | 54.1 |
| 550°F+ | 25.1 | 25.9 |
| C1-C4 Gas | 1.97 | 4.38 |
| Total | 102.1 | 102.1 |

TABLE 21

INSPECTION OF JP-8 PRODUCTS

| <u>Requirements</u> | <u>JP-8 Specification</u> | <u>JP-8 HT Inspection</u> | <u>JP-8 HC Inspection</u> |
|---------------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Color, Saybolt | Report | | |
| Total Acid Number, mg KOH/gm, max. | 0.015 | | |
| Aromatics, Vol%, max. | 25.0 | 23.5 | 20.0 |
| Olefins, Vol%, max. | 5.0 | 1.5 | 1.5 |
| Sulfur, Mercaptan, Wt%, max. | 0.001 | 0.000 | 0.000 |
| Sulfur, Total, Wt%, max. | 0.4 | 0.0 | 0.0 |
| Distillation Temperature, °C | | | |
| Initial Boiling Point | Report | | |
| 10% Recovered, max. | 205 | | |
| 20% Recovered, max. | Report | | |
| 50% Recovered, max. | Report | | |
| 90% Recovered, max. | Report | | |
| End Point, max. | 300 | | |
| Residue, Vol%, max. | 1.5 | | |
| Loss, Vol%, max. | 1.5 | | |
| Flash Point, °C, max. | 38 | 33 | 27 |
| Gravity, °API or | 37-51 | -- | -- |
| Density, kg/m ³ at 15°C | 775-840 | 850 | 832 |
| Freezing Point, °C, max. | -50 | -50 | -50 |
| Viscosity at -20°C, C'stokes, max. | 8.0 | 1.45@100°F | 1.42@100°F |
| Net Heat of Combustion, MJ/kg min. | 42.8 | | |
| Combustion: | | | |
| (1) Hydrogen Content, wt% min., | 13.6 | -- | -- |
| or (2) Smoke Point, mm min. | 25 | -- | -- |
| or (3) Smoke point, mm min. and | 20 | 22 | 20 |
| Napthalenes, Vol% max. | 3.0 | 0.73 | 0.70 |
| Copper Strip Corrosion, | 1b | 1a | 1a |
| 2 Hr @ 100°C (212°F) | | | |
| Thermal Stability: | | | |
| Change in Pressure Drop, mm Hg max. | 25 | 1 | 1 |
| Heater Tube Deposit Visual Rating | Less than Code 3 | -2 | -2 |
| Existent Gum, mg/100 ml, max. | 7.0 | 4.8 | 5.2 |
| Particulate Matter, mg/Liter, max. | 1.0 | -- | -- |
| Water Separation Index, Modified min. | 70 | 89 | 87 |
| Fuel System Icing Inhibitor, Vol% | 0.10-0.15 | -- | -- |

Note: "HC" product contains hydrotreated and hydrocracked stocks;
 "HT" product contains only hydrotreated stock.

Both samples were treated over Fluorex LVM clay in a 2 inch diameter by 12 inch high column at a velocity of 1.0 feet per minute before adding 2.8 ppm of UOP U-344 antioxidant. The benefits of clay treatment may be seen by comparing these with properties of the untreated fuels shown in Table 15. Apparently, the clay removes gums and acidity to improve existent gum, copper strip corrosion, and water separation index results.

All of the specifications for JP-8 were met, except the flash point of both samples are low because too much low boiling material was added during blending. The low boiling material was added to satisfy the density requirement. Also, the HT fuel failed the density specification because no lower-density hydrocrackate was added.

The high density of these fuels is attributed to operation of the second hydrotreater at higher throughputs than specified in the recommended design during the pilot plant run, primarily to expedite production. The aromatics content of product hydrotreated at the correct rate would have been lower, allowing the final product to meet both density and flash point requirements.

SECTION VI

SUMMARY AND CONCLUSIONS

After initial experiments in Task 2 failed to confirm the plan outlined in Task 1, development of a viable process became the primary objective. Bench scale experiments provided the basis for an improved process plan, established pilot plant conditions for Task 3 and a preliminary design basis for Task 4, and produced small quantities of JP-8, JP-8X, and JP-4 jet fuels.

In the improved process, a distillation pretreatment step removes heteroatom-containing light ends from the tar oil feed to reduce hydrogen consumption, decreasing jet fuel cost by about 2 percent. It was necessary to add a second hydrotreating stage to decrease aromatics to the level specified for jet fuels.

Pilot plant operation in Task 3 confirmed the viability of the Task 2 process by demonstrating extensive recycle of high boiling materials in the hydrocracker. Two barrels of JP-8 jet fuel were produced for evaluation by the Air Force.

Optimization, particularly the data analysis outlined in the Contract for confirming the reaction kinetics used in the Task 1 models, was not completed. Instead efforts were focused on developing a viable process. However, the raw data necessary for this analysis are presented herein, and these were used to specify the process design conditions.

SECTION VII

RECOMMENDATIONS

Hydrocracking experiments suggested that coal-derived liquids deactivate catalysts more rapidly than petroleum-derived stocks. This should be verified and the cause determined. Examination of heteroatomic species distributions (particularly nitrogen) would be the logical starting point.

The information from Tasks 2 and 3 provide sufficient data to evaluate a preliminary design basis for the production of JP-8 from the Great Plains tar oil. These data should be used in Tasks 4 and 5.

REFERENCES

1. Smith, E. B., "Jet Fuels from Coal; Third Quarterly Report," U.S. Department of Energy Research Contract No. DE-FC21-86MC11076, May 1987.
2. Sinor, J. E., "Production of Jet Fuel from Coal-Derived Liquids, Vol 1, Market Assessment for Liquid By-Products from the Great Plains Gasification Plant," AFWAL-TR-87-2042, August 1987.
3. Fleming, B. A., et al., "Production of Jet Fuels From Coal-Derived Liquids, Vol VI, Preliminary Analysis of Upgrading Alternatives for the Great Plains Liquid By-Product Streams," AFWAL-TR-87-2042, September 1988.
4. U.S. Department of Energy, Contract No. DE-RP-22-86PC90015, "Production of Jet Fuel from Coal-Derived Liquids," Effective May 1, 1987.
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APPENDIX A

BRIEF DESCRIPTION OF LCI PILOT PLANT

APPENDIX A

BRIEF DESCRIPTION OF LCI PILOT PLANT

FEED SYSTEMS

The total hydrogen flow is measured using an orifice meter. The individual hydrogen feed rates to the reactor, instrument sensing lines, etc., are measured with rotameters. All the catalytic hydrogen is introduced at the bottom of the reactor.

The oil feed is metered into the reactor loop using a positive displacement pump. The feed rate is monitored by measuring the weight loss in the run tank which is mounted on an electronic scale.

EXPANDED BED REACTOR

The LC-Fining reactor system consists of (1) a two-stage, expanded-bed in series reactor system, (2) a recycle surge bomb for each reactor stage, and (3) a duplex remote head recycle pump for each reactor stage. The liquid hourly space velocity is calculated based on either the total thermal reactor volume including the recycle lines and surge bomb or on the settled-bed catalyst volume. The reactor and reactor loop are heated electrically with nine temperature controlled circuits for each reactor stage, which provide almost isothermal operation.

The internal recycle rate is set to provide a bed expansion of 10-35% depending upon catalyst and feed properties. The connecting line to the remote check assembly is purged intermittently with a small quantity of gas oil from the stripping column.

RECOVERY SECTION

The net liquid and gas from the reactor loop are separated in the high temperature-high pressure (HT-HP) separator. The light oil overhead from the HT-HP separator is condensed and collected in the low temperature-high pressure (LT-HP) separator where it is removed by level control. Quench water is introduced periodically upstream of the condenser to prevent the buildup of sulfides in the lines. The quench water is taken off in a decanter following the LT-HP level controller. The vapors from the LT-HP separator pass through the main pressure control valve which reduces the pressure to atmospheric. The low pressure gas is chilled, scrubbed, sampled, metered and vented. The hydrogen is not recycled back to the reactors.

The heavy oil from the HT-HP separator is let down through the level control valve to the low pressure-high temperature separator, which is maintained at about 55 psig. The net flow of heavy oil through the recovery section is low. Heavy oil is recycled from the HT-LP separator back to the HT-HP separator to (1) eliminate dead spots which may lead to overheating or phase separation and (2) increase the flow through the level control valve. A small quantity of stripping gas is introduced into the separator to remove a fraction of the gas oil from the heavy oil. The vapors from the HT-LP separator are let down to atmospheric pressure and stripped. The stripped gas oil, removed from the

stripper by level control, is combined with stripper overhead product and the liquid from the cold trap to form the light oil product. The heavy oil is removed from the HT-LP separator by level control, collected and weighed on an electronic scale.

SAMPLING AND OPERATING PROCEDURE

Daily operations are usually divided into 12-hour test periods. Routine maintenance and changes in operating conditions are usually made during the day shift. The cold trap liquid is blended in with the light oil receiver liquid prior to analysis. The gas analysis is done on a composite of equal volume hourly samples. The hydrogen consumption is calculated from the normalized feed and product elemental analyses. The yields of H_2S , NH_3 and H_2O are usually obtained from the elemental balances for sulfur, nitrogen and oxygen, respectively.

REACTOR LOOP

Total Volume: 1.38 Gallon /stage

Pressure: 2000 psig

HIGH TEMPERATURE- PRESSURE SEPARATOR

Pressure: 2000 psig

HIGH TEMPERATURE- LOW PRESSURE SEPARATOR

Pressure: 50 psig

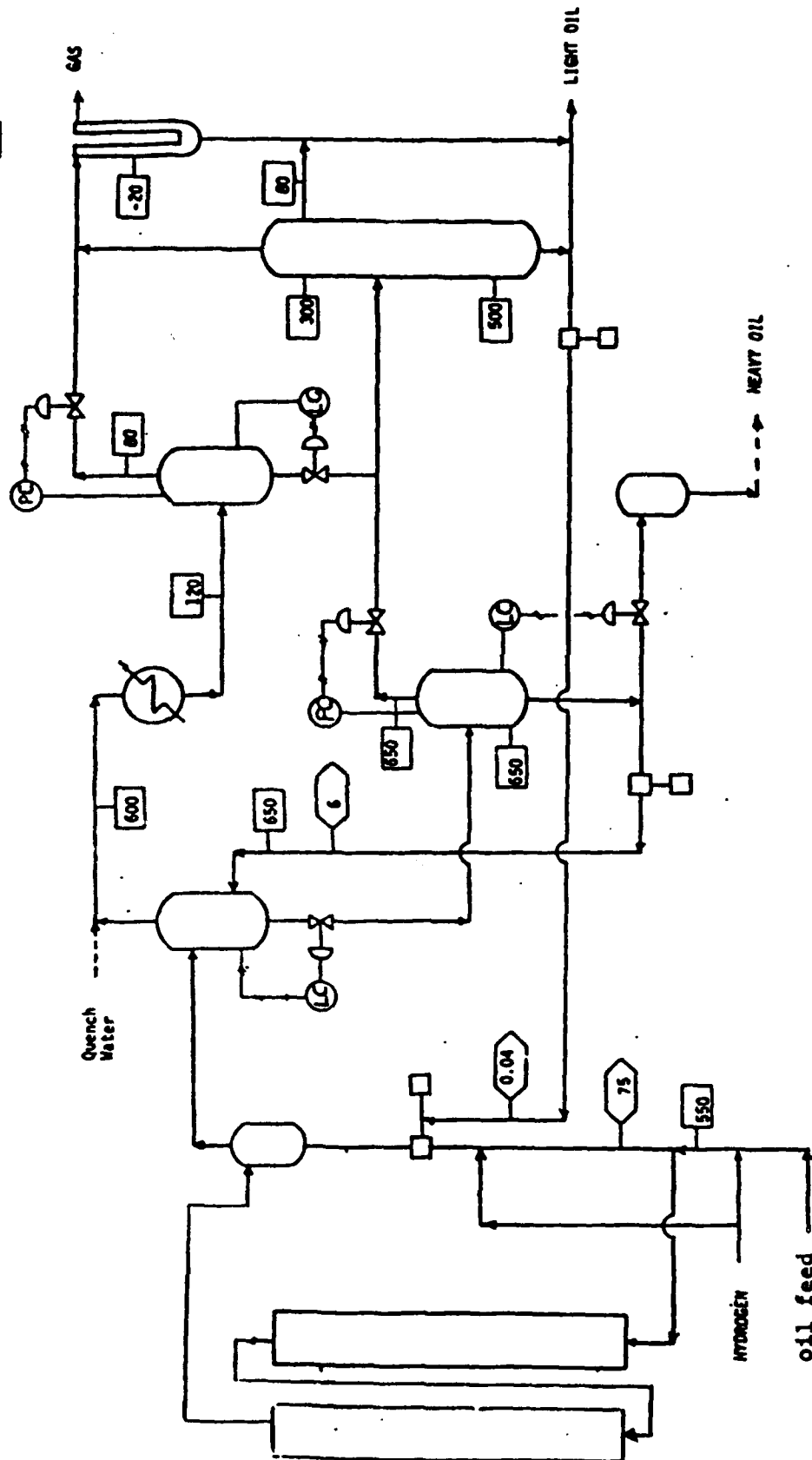
LOW TEMPERATURE- HIGH PRESSURE SEPARATOR

Pressure: 2000 psig

LIGHT OIL STRIPPER

Pressure: 0 psig

COLD
TRAP



□ Nominal
Temperature, °F
⬡ Nominal
Flow Rate, GPH

LCI PILOT PLANT CONFIGURATION

LCI TEST REPORT ON EXPANDED-BED
HYDROPROCESSING OF 300°F+ GREAT PLAINS TAR OIL

Summary

The six drums (300 gal.) of Great Plains 300°F+ tar oil supplied by Amoco were successfully hydrotreated in LCI's two-stage, expanded bed pilot plant. The tar oil was processed over a twelve-day period at operating conditions recommended by Amoco. The objective of the hydrotreatment was to reduce the nitrogen and other heteroatoms and to maximize hydrogen uptake. These objectives were achieved. The daily nitrogen removals ranged from 95% to 99%. After blending by Amoco, the composited total liquid product should have a nitrogen content of about 150 to 200 ppm. The hydrogen consumption for the entire run averaged about 3200 SCF/bbl. The operating conditions, product properties, yields and conversions for each of the twelve operating days are attached. Six drums of the hydrotreated product were sent to your attention along with the daily 1 quart total liquid product (TLP) samples.

Pilot Plant Operation and Results

A general description of the LC-Fining pilot plant equipment and the sampling and operating procedure have already been provided in earlier communications and will not be repeated here. A brief summary of this specific pilot plant run is given below.

Each of the two LC-Fining reactors was charged with 3500 cc of dried, screened Shell 324 M catalyst. The total catalyst charged was 5760 gms which was used as the basis for the weight hourly space velocity calculation. The catalyst was presulfided with 5% HS_2/H_2 at 400°F to 700°F over a 16-hour period following a standard procedure for Shell catalysts. After cooling to 500°F and increasing the pressure to 1500 psig, the tar oil feed was started and adjusted to achieve 0.6 WHSV. The reactor temperatures were increased to 700°F and maintained there for the first day, pending analytical results. As shown in the attached results, the TLP nitrogen content was 365 ppm. This was higher than the 200 ppm N desired by Amoco. The reactor temperatures were increased to 760°F and the total pressure was increased to 2000 psig while the space velocity was maintained at 0.6 hr^{-1} . The TLP nitrogen was reduced to 90 ppm. The hydrogen uptake had increased from 2900 SCF/bbl to 3600 SCF/bbl. This exceeded the product specification and in order to process the maximum amount of material in the allotted time, the space velocity was increased to 0.8 hr^{-1} . At these conditions the TLP nitrogen was 151 ppm and the hydrogen uptake was 3200 SCF/bbl.

During period 3, the recycle pump on the first reactor shut off (due to electrical high temperature shutoff). The bottom reactor temperature increased to more than 930°F before the pump could be restarted. Since about 2 gal. decant oil had to be added to the pump connecting lines following this incident, the product for the next 6 hours was taken offstream and was not included in the drummed product. There was some increase in the ΔP across the reactor following the high temperature excursion and it was thought this might be due to coke formation. However, inspection of the reactor after the run indicated that the pressure drop was primarily due to catalyst which had worked its way through the distributor and into the bottom screen.

LCI TEST REPORT ON EXPANDED-BED HYDROPROCESSING
OF 300F+ GREAT PLAINS TAR OIL

The TLP nitrogen for period 4 at 0.64 WHSV was 134 ppm so the space velocity was increased to 0.7 hr^{-1} and then 0.75 hr^{-1} for periods 5 and 6, respectively. During period 8 about 2 quarts decant oil was added to the recycle pump connecting lines accounting for the 104% material balance for the period. This product was kept isolated so Amoco could choose whether or not to blend it. The space velocity was maintained at 0.75 hr^{-1} up to period 9 when, after the TLP nitrogen had increased to 275 ppm, it was reduced to 0.65 hr^{-1} for the remainder of the run.

Throughout the run the recycle line was maintained about 20°F cooler than the reactor temperature. This in combination with the high recycle rate (35-40 gal/hr) facilitated removal of the exothermic heat and provided very effective and stable temperature control. Except for the loss of the recycle pump during period 3, no problems were encountered in controlling the reaction exotherm.

By V. A. Strangio
V. A. Strangio

Approved M. I. Greene
M. I. Greene

Job No. 5-2730

Date: August 25, 1988

**FEEDSTOCK INSPECTION
COAL DERIVED LIQUIDS**

| | LCI | AMOCO |
|-----------------------|--------|--------|
| ===== | ===== | ===== |
| SAMPLE NUMBER | 3602 | |
| DESCRIPTION | 300 F+ | |
| ----- | ----- | ----- |
| GRAVITY, DEG API | 5.1 | 6.6 |
| SP.GR. @ 60/60 | 1.0359 | 1.028 |
| ELEMENTAL ANALYSIS | | |
| CARBON, WT% | 84.29 | 84.71 |
| HYDROGEN, WT% | 8.55 | 8.60 |
| SULFUR, WT% | 0.42 | 0.49 |
| NITROGEN, PPM | 7309 | 7283 |
| OXYGEN, WT% (BY DIFF) | 6.01 | 5.47 |
| ----- | ----- | ----- |
| TOTAL | 100.00 | 100.00 |
| ----- | ----- | ----- |
| SIMDIS (WT%) | | |
| IBP | * 335 | 279 |
| 5 | 375 | 336 |
| 10 | 402 | 371 |
| 20 | 434 | 414 |
| 30 | 482 | 468 |
| 40 | 540 | 498 |
| 50 | 591 | 556 |
| 60 | 653 | 603 |
| 70 | 733 | 683 |
| 80 | 825 | 765 |
| 90 | 943 | 877 |
| 95 | 1024 | 948 |
| FBP | 1212 | 1018 |
| ----- | ----- | ----- |

* SIMDIS was calibrated with pure aromatic standards. It was not calibrated for this particular feedstock. These SIMDIS values should be used only for relative comparisons with the products.

DAILY EXPERIMENTAL RESULTS

| PERIOD NUMBER | 1 | 2 | 3 | 4 | |
|--------------------------------|--------|--------|--------|--------|------|
| DATE | 1988 | 8/10 | 8/11 | 8/12 | 8/13 |
| TEMPERATURE, DEG F | | | | | |
| FIRST STAGE TOP | 691 | 758 | 789 | 761 | |
| " " MID | 687 | 759 | 796 | 766 | |
| " " BOT | 666 | 740 | 757 | 744 | |
| SECOND STAGE TOP | 700 | 754 | 765 | 750 | |
| " " MID | 694 | 743 | 761 | 751 | |
| " " BOT | 673 | 733 | 745 | 738 | |
| TOTAL PRESSURE, PSIG | 1500 | 2000 | 2000 | 2000 | |
| WHSV, LBS/LB/HR | .63 | .597 | .802 | .635 | |
| CATALYTIC H2, SCF/BBL | 7300 | 7700 | 5700 | 7200 | |
| CARBON BALANCE, WT% RECOVERY | 97 | 96 | 99 | 100 | |
| MATL. BALANCE, WT% RECOVERY | 100 | 101 | 100 | 101 | |
| TLP PROPERTIES | | | | | |
| API GRAVITY | 27.3 | 31.6 | 30.2 | 29.4 | |
| CARBON, WT% | 87.70 | 86.93 | 87.60 | 87.52 | |
| HYDROGEN, WT% | 12.17 | 12.89 | 12.37 | 12.46 | |
| SULFUR, WT% | 0.03 | 0.01 | 0.01 | 0.01 | |
| NITROGEN, PPM | 365 | 90 | 151 | 134 | |
| OXYGEN, WT% (BY DIF) | 0.06 | 0.16 | 0.00 | 0.00 | |
| TOTAL | 100.00 | 99.99 | 99.98 | 99.99 | |
| * SIMDIS (WT%) | | | | | |
| IBP | 194 | 178 | 172 | 176 | |
| 10 | 286 | 259 | 249 | 253 | |
| 20 | 364 | 337 | 323 | 325 | |
| 30 | 406 | 380 | 379 | 385 | |
| 40 | 458 | 423 | 419 | 430 | |
| 50 | 508 | 468 | 469 | 476 | |
| 60 | 561 | 518 | 515 | 528 | |
| 70 | 633 | 577 | 572 | 597 | |
| 80 | 718 | 656 | 653 | 676 | |
| 90 | 853 | 775 | 779 | 797 | |
| FBP | 1146 | 1049 | 1075 | 1060 | |
| 550 F+ (WT%) | 41.8 | 34.0 | 33.3 | 36.2 | |
| DAILY PRODUCT YIELDS, WT% FEED | | | | | |
| OFFGAS H2S (CALC) | 0.42 | 0.44 | 0.44 | 0.44 | |
| OFFGAS NH3 (CALC) | 0.85 | 0.88 | 0.87 | 0.87 | |
| OFFGAS H2O (CALC) | 6.69 | 6.59 | 6.76 | 6.76 | |
| OFFGAS C1 | 0.36 | 1.61 | 0.64 | 0.56 | |
| OFFGAS C2 | 0.00 | 0.62 | 0.95 | 0.77 | |
| OFFGAS C3 | 0.22 | 0.92 | 0.44 | 0.40 | |
| OFFGAS C4 | 0.16 | 0.52 | 0.46 | 0.41 | |
| OFFGAS C5+ | 0.40 | 0.99 | 1.43 | 0.80 | |
| TLP | 95.07 | 92.69 | 92.60 | 93.60 | |
| TOTAL | 104.16 | 105.26 | 104.58 | 104.61 | |
| H2 CONSUMPTION, SCF/BBL | | | | | |
| WT% 550 F+ CONVERSION | 32 | 46 | 47 | 42 | |
| % DESULFURIZATION | 93 | 98 | 98 | 98 | |
| % DENITROGENATION | 95 | 99 | 98 | 98 | |
| % DEOXYGENATION | 99 | 98 | 100 | 100 | |

* SIMDIS to be used for relative comparisons only.

DAILY EXPERIMENTAL RESULTS

| PERIOD NUMBER | 5 | 6 | 7 | 8 | |
|--------------------------------|------|--------|--------|--------|--------|
| DATE | 1988 | 8/14 | 8/15 | 8/16 | 8/17 |
| TEMPERATURE, DEG F | | | | | |
| FIRST STAGE TOP | | 758 | 756 | 761 | 754 |
| " " MID | | 761 | 751 | 759 | 754 |
| " " BOT | | 730 | 729 | 730 | 725 |
| SECOND STAGE TOP | | 756 | 755 | 755 | 754 |
| " " MID | | 751 | 750 | 748 | 751 |
| " " BOT | | 737 | 738 | 737 | 735 |
| TOTAL PRESSURE, PSIG | | 2000 | 2000 | 2000 | 2000 |
| WHSV, LBS/LB/HR | | .718 | .751 | .752 | .736 |
| CATALYTIC H2, SCF/BBL | | 6400 | 6100 | 6100 | 6200 |
| CARBON BALANCE, WT% RECOVERY | | 99 | 97 | 97 | 104 |
| MATL. BALANCE, WT% RECOVERY | | 100 | 98 | 98 | 104 |
| TLP PROPERTIES | | | | | |
| API GRAVITY | | 28.8 | 28.8 | 28.8 | 28.2 |
| CARBON, WT% | | 87.53 | 87.56 | 87.77 | 87.32 |
| HYDROGEN, WT% | | 12.42 | 12.40 | 12.55 | 12.27 |
| SULFUR, WT% | | 0.01 | 0.01 | 0.01 | 0.01 |
| NITROGEN, PPM | | 155 | 161 | 199 | 250 |
| OXYGEN, WT% (BY DIF) | | 0.02 | 0.01 | 0.00 | 0.38 |
| TOTAL | | 100.00 | 100.00 | 100.35 | 100.00 |
| * SIMDIS (WT%) | | | | | |
| IBP | | 178 | 178 | 172 | 174 |
| 10 | | 255 | 254 | 256 | 258 |
| 20 | | 330 | 328 | 333 | 342 |
| 30 | | 388 | 388 | 394 | 396 |
| 40 | | 435 | 436 | 443 | 451 |
| 50 | | 481 | 484 | 492 | 501 |
| 60 | | 532 | 537 | 543 | 552 |
| 70 | | 605 | 612 | 617 | 626 |
| 80 | | 683 | 691 | 695 | 707 |
| 90 | | 810 | 824 | 825 | 831 |
| FBP | | 1083 | 1105 | 1093 | 1088 |
| 550 F+ (WT%) | | 37.0 | 37.7 | 38.8 | 40.4 |
| DAILY PRODUCT YIELDS, WT% FEED | | | | | |
| OFFGAS H2S (CALC) | | 0.44 | 0.44 | 0.44 | 0.44 |
| OFFGAS NH3 (CALC) | | 0.87 | 0.87 | 0.86 | 0.86 |
| OFFGAS H2O (CALC) | | 6.73 | 6.75 | 6.76 | 6.36 |
| OFFGAS C1 | | 0.52 | 0.51 | 0.52 | 0.51 |
| OFFGAS C2 | | 0.58 | 0.44 | 0.44 | 0.34 |
| OFFGAS C3 | | 0.37 | 0.36 | 0.36 | 0.35 |
| OFFGAS C4 | | 0.39 | 0.37 | 0.35 | 0.37 |
| OFFGAS C5+ | | 1.11 | 0.68 | 0.99 | 0.94 |
| TLP | | 93.56 | 94.10 | 93.58 | 94.20 |
| TOTAL | | 104.57 | 104.51 | 104.30 | 104.37 |
| H2 CONSUMPTION, SCF/BBL | | 3100 | 3100 | 3200 | 3000 |
| WT% 550 F+ CONVERSION | | 41 | 39 | 39 | 35 |
| % DESULFURIZATION | | 98 | 98 | 98 | 98 |
| % DENITROGENATION | | 98 | 98 | 97 | 97 |
| % DEOXYGENATION | | 100 | 100 | 100 | 94 |

* SIMDIS to be used for relative comparisons only.

DAILY EXPERIMENTAL RESULTS

| PERIOD NUMBER | 9 | 10 | 11 | 12 |
|--------------------------------|--------|--------|--------|--------|
| DATE | 1988 | 8/18 | 8/19 | 8/20 |
| TEMPERATURE, DEG F | | | | |
| FIRST STAGE TOP | 760 | 756 | 762 | 762 |
| " " MID | 758 | 751 | 761 | 760 |
| " " BOT | 728 | 729 | 738 | 739 |
| SECOND STAGE TOP | 754 | 755 | 754 | 753 |
| " " MID | 748 | 750 | 749 | 748 |
| " " BOT | 734 | 738 | 735 | 734 |
| TOTAL PRESSURE, PSIG | 2000 | 2000 | 2000 | 2000 |
| WHSV, LBS/LB/HR | .732 | .636 | .648 | .667 |
| CATALYTIC H2, SCF/BBL | 6300 | 7200 | 7100 | 6900 |
| CARBON BALANCE, WTX RECOVERY | 98 | 96 | 97 | 100 |
| MATL. BALANCE, WTX RECOVERY | 99 | 97 | 98 | 101 |
| TLP PROPERTIES | | | | |
| API GRAVITY | 29 | 29.2 | 29.4 | 29 |
| CARBON, WTX | 87.27 | 87.86 | 87.27 | 87.57 |
| HYDROGEN, WTX | 12.33 | 12.63 | 12.36 | 12.40 |
| SULFUR, WTX | 0.01 | 0.01 | 0.01 | 0.01 |
| NITROGEN, PPM | 275 | 178 | 92 | 148 |
| OXYGEN, WTX (BY DIF) | 0.36 | 0.00 | 0.35 | 0.01 |
| TOTAL | 100.00 | 100.52 | 100.00 | 100.00 |
| * SIMDIS (WTX) | | | | |
| IBP | 174 | 174 | 175 | 175 |
| 10 | 257 | 254 | 254 | 256 |
| 20 | 336 | 333 | 329 | 333 |
| 30 | 396 | 393 | 392 | 393 |
| 40 | 446 | 442 | 440 | 443 |
| 50 | 495 | 490 | 486 | 491 |
| 60 | 544 | 540 | 536 | 540 |
| 70 | 616 | 612 | 605 | 610 |
| 80 | 693 | 690 | 682 | 687 |
| 90 | 822 | 814 | 803 | 810 |
| FBP | 1084 | 1078 | 1062 | 1076 |
| 550 F+ (WTX) | 39.0 | 38.3 | 37.6 | 38.2 |
| DAILY PRODUCT YIELDS, WTX FEED | | | | |
| OFFGAS H2S (CALC) | 0.44 | 0.44 | 0.44 | 0.44 |
| OFFGAS NH3 (CALC) | 0.86 | 0.87 | 0.88 | 0.87 |
| OFFGAS H2O (CALC) | 6.38 | 6.76 | 6.39 | 6.75 |
| OFFGAS C1 | 0.51 | 0.51 | 0.62 | 0.58 |
| OFFGAS C2 | 0.41 | 0.47 | 0.52 | 0.39 |
| OFFGAS C3 | 0.36 | 0.35 | 0.42 | 0.40 |
| OFFGAS C4 | 0.35 | 0.35 | 0.41 | 0.42 |
| OFFGAS C5+ | 1.13 | 1.02 | 1.17 | 1.06 |
| TLP | 94.02 | 93.45 | 93.68 | 93.63 |
| TOTAL | 104.45 | 104.21 | 104.52 | 104.54 |
| H2 CONSUMPTION, SCF/BBL | 3100 | 3200 | 3100 | 3100 |
| WTX 550 F+ CONVERSION | 37 | 39 | 40 | 39 |
| % DESULFURIZATION | 98 | 98 | 98 | 98 |
| % DENITROGENATION | 96 | 98 | 99 | 98 |
| % DEOXYGENATION | 94 | 100 | 95 | 100 |

* SIMDIS to be used for relative comparisons only.